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ERRATUM

Vol. 32, pp. 685 and 710. In the printing of the July issue of this Journal, the illustrations (Fig. 1) in the papers by Edwards and Singh and by Edwards, Marion, and McIvor were transposed. The figure that appears on p. 685 should be on p. 710 and the figure on p. 710 should be on p. 685. The two loose sheets enclosed in this issue of the Journal have been reprinted to include the correction and should be inserted in place of pp. 685 and 686 and pp. 709 and 710 in the July issue.

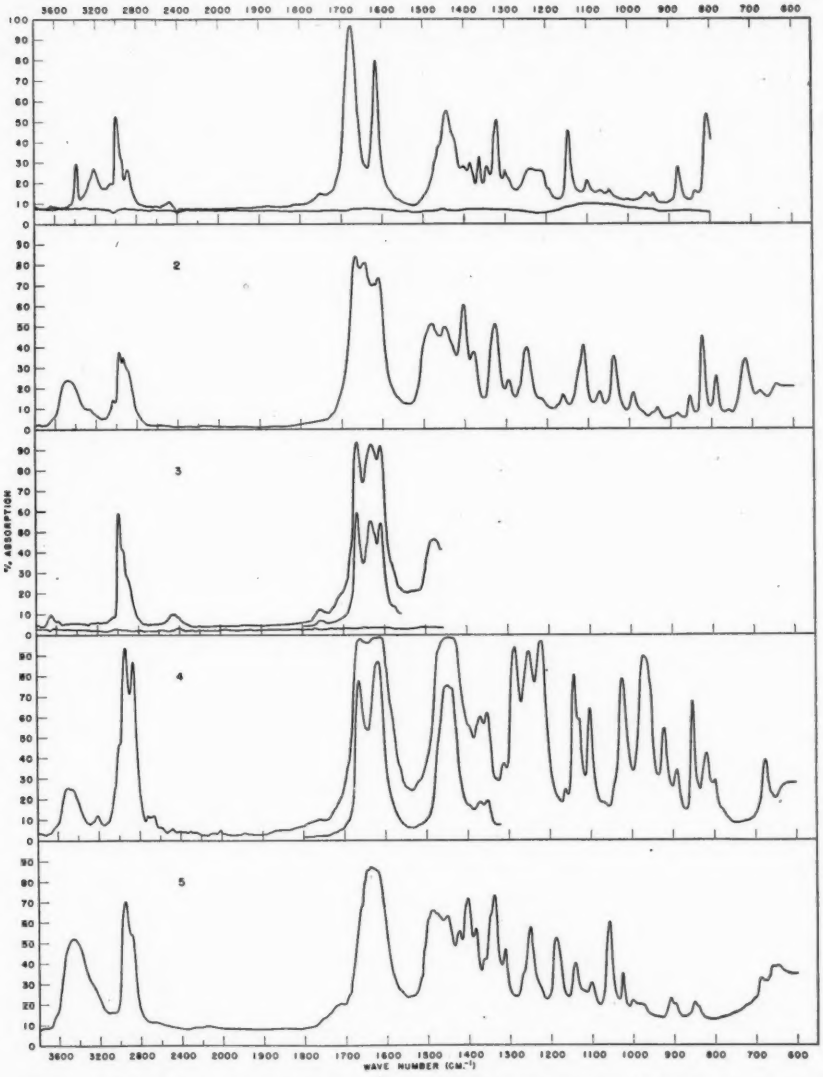


FIG. 1. Infrared spectra of: 1. 6-methyl-5,6-dihydro-2-pyridone (chloroform), 2. 1,6-dimethyl-5,6-dihydro-2-pyridone (liquid), 3. 1,6-dimethyl-5,6-dihydro-2-pyridone (chloroform), 4. N-crotonylpiperidine (liquid), 5. 1,6-dimethyl-2-piperidone (liquid). The background trace in 1 and 3 is that obtained when both cells were filled with pure chloroform.

in the 1600–1700 cm.$^{-1}$ region (Fig. 1). No bands occur in the 1500–1600 cm.$^{-1}$ region in the saturated or unsaturated lactams.

The C=C and C=O stretching bands in the α–β unsaturated amides would be expected to lie in the 1610–1630 cm.$^{-1}$ region since conjugation usually shifts

This page has been reprinted to include the correction pointed out in the Errata that appear at the end of the volume.

both toward smaller wave numbers. The C=C band should as usual be very much weaker than the C=O band. The CN band according to Letaw and Gropp (10) should lie between 1600 and 1650 cm.$^{-1}$. A possible explanation of the spectra actually found is that the three vibrations have very close to the same fundamental frequency, and that resonance between them results in split bands of higher and lower frequency with very much modified relative intensity.

The "iso" compounds derived from lycoctonine have single bands near 1650 cm.$^{-1}$ which lends no support to the unsaturated lactam suggestion.

The infrared spectra of bakankosine derivatives resemble that of N-crotonyl-piperidine more than that of 6-methyl-5,6-dihydro-2-pyridone (the 1610 cm.$^{-1}$ band is more intense than the 1670 cm.$^{-1}$ band). However, the alkaloid spectra could as readily be interpreted as that of α–β unsaturated ketones (1670 cm.$^{-1}$) with an isolated hydrogen bonded lactam (1610 cm.$^{-1}$). (See the discussion of ultraviolet spectra.)

The hydrogen on the double bonds (*cis* disubstituted in I and II) shows up in the infrared near 3040 cm.$^{-1}$ (CH stretching) and probably (3) in the strong band at 805–820 cm.$^{-1}$ (CH bending). It is interesting that the 3040 band does not appear in the spectrum of the N-alkyl lactam II taken in chloroform.

The band at 2800 cm.$^{-1}$ in 4-methylamino-1,6-dimethyl-2-piperidone can most probably be assigned to the C–H stretching of the methyl group on the basic nitrogen since the N-methyl lactams do not show it.

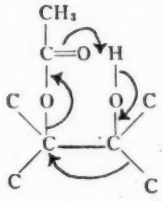
The 3400–3500 cm.$^{-1}$ bands in the spectra of liquid films of N-dialkyl amides have been noted by Letaw and Gropp (10). They consider them to be overtones of the 1600–1700 cm.$^{-1}$ bands. We have observed with lupanine (4) and in the present work that this band does not appear in the spectra in chloroform or carbon disulphide solutions. It is much too intense for an overtone, and in addition, it is at too high a wave number (first overtones usually appear at a wave number very close to double the parent wave number). Thus the only simple explanation of this band appears to be that in the liquid state N-alkyl lactams exist to a considerable extent as the enol. Although lupanine gave no methane in the Zerewitinoff determination, freshly distilled II and 1,6-dimethyl-2-piperidone gave close to one mole at 100°, indicating the mobility of the hydrogens α (or γ) to the carbonyls.

The two lactams with an NH (I and 2-piperidone) in chloroform solution had sharp bands near 3400 cm.$^{-1}$ (free NH) and broader bands of similar intensity near 3200 cm.$^{-1}$ (bonded NH). In the spectra of the pure substances, however, the 3400 cm.$^{-1}$ band was absent but the 3200 cm.$^{-1}$ one was much more intense.

A study of saturated N-alkyl lactams in which enolization is blocked by alkyl substitution, or which contain N^{15}, and α–β unsaturated N-alkyl lactams with the double bond carbons substituted might clarify the origin of the infrared spectra in the 3 and 6μ regions.

A summary of the position of the bands in the 1600–1700 cm.$^{-1}$ region of some saturated and α–β unsaturated six-membered lactams is given in Table II.

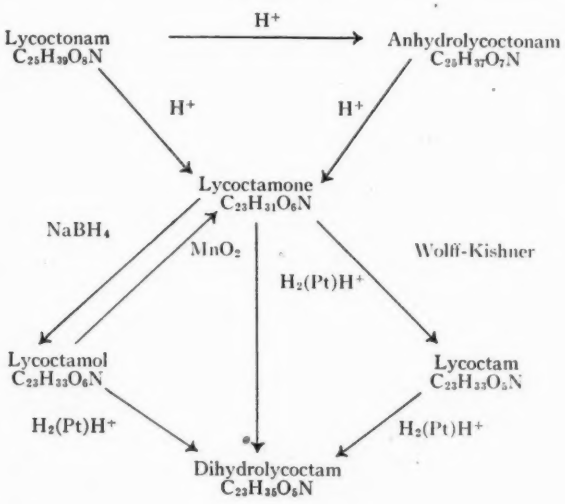
methoxyl, should be less basic than the one on the larger ring. Thus on this basis alone, the pinacolic dehydration would be expected to give II. However, on the basis of the considerations of Brown and co-workers (3) it appears likely that the hydroxyl on the five-membered ring would be more readily eliminated, giving the more stable cyclopentyl carbonium ion. This would give rise to I on rearrangement. The same conclusion is reached on consideration of the pyrolysis of des(oxymethylene)-lycoctonam monoacetate (4). Since the cyclopentanone carbonyl in the diketones derived from lycoctonine derivatives is much less hindered than that on the larger ring (5), it is reasonable to suppose that the same relative hindrance exists for the hydroxyls in the parent glycol. Hence the above acetate should involve the hydroxyl on the five-membered ring. Since the pyrolysis most likely proceeds as shown,



the product would again be I, making this seem the more likely possibility.

Anhydrolycoctonam could be recovered unchanged after attempted Wolff-Kishner reduction, hence the carbonyl is very hindered. In concordance with this, the carbonyl is only slowly reduced by sodium borohydride. The hydroxyl derived from the ketone in this reduction could be acetylated readily, however, giving an acetate which did not lose acetic acid readily at 290°. These observations, and the fact that the ketone was inert to selenium dioxide in

FLOWSHEET



refluxing acetic acid, suggest that the other carbon α to the carbonyl is tertiary or perhaps quaternary.

On more vigorous treatment with acid, lycoctonam and anhydrolycoctonam undergo extensive change. One methoxyl is hydrolyzed to a tertiary hydroxyl

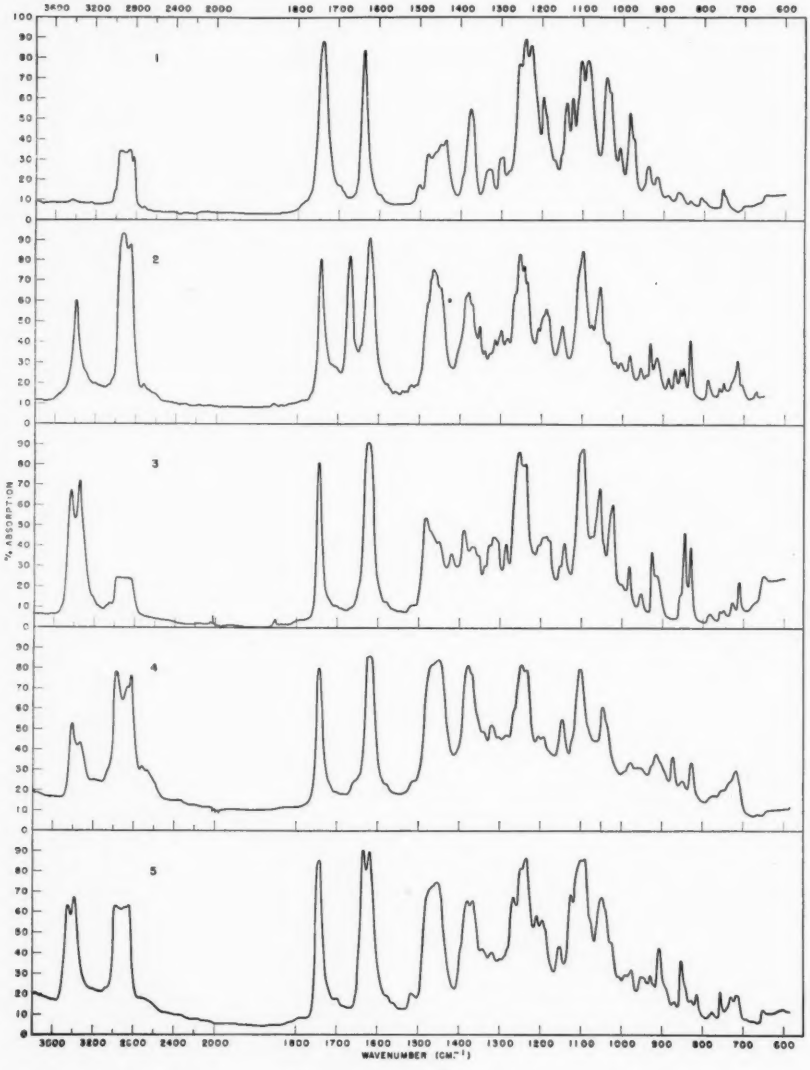


FIG. 1. Infrared spectra (nujol mulls): 1. Dihydroanhydrolycoctonam diacetate. 2. Lycoctamone monoacetate. 3. Lycoctamol monoacetate. 4. Lycoctam monoacetate. 5. Dihydrolycoctam monoacetate.

This page has been reprinted to include the correction pointed out in the Errata that appear at the end of the volume.

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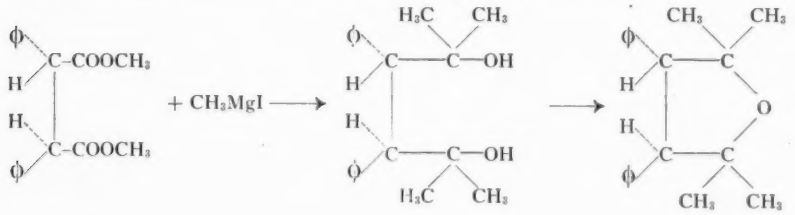
ROTAMERISM DURING DEMETHYLATION OF THE 2,5-DIMETHOXY-2,5-DIMETHYL-3,4-DIPHENYLHEXANES[1]

BY J. G. SMITH AND GEORGE F WRIGHT

ABSTRACT

The fission of methanol from the diastereomeric 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexanes leads to products which are best explained in terms of restriction about the central carbon–carbon bond. As would be expected from its stable conformation the *dd,ll* diastereomer easily forms the 2,2,5,5-tetramethyl-3,4-diphenyltetrahydrofuran, but the *meso* diastereomer forms a tetrahydrofuran with difficulty. On the other hand the *meso* diastereomer readily undergoes Friedel-Crafts types of condensation leading in different media to either 3,3-dimethyl-1-isopropenyl-2-phenylindane, 3,3-dimethyl-1-isopropyl-2-phenylindene or 5,5,10,10-tetramethyl-4*b*,5,9*b*,10-tetrahydroindeno[2,1-*a*]-indene. These indenes are the expected products from a consideration of the conformation of the *meso*-dimethoxydimethyldiphenylhexane which is most free from steric restriction.

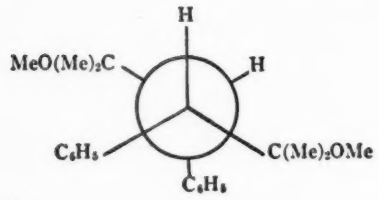
The two possible diastereomers of 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane have been reported (1). One is a liquid (IV), very viscous, which has resisted attempts to cause it to crystallize during three years. Treatment with a variety of acidic demethylating agents forms only one product, 2,2,5,5-tetramethyl-3,4-diphenyltetrahydrofuran (III). This cyclic ether has been prepared by methylation of the corresponding diol II which was synthesized from dimethyl *dd,ll*-diphenylsuccinate (I) and methyl iodide Grignard reagent, and the oil (IV) therefore must have the same *dd,ll* configuration (3). The ease



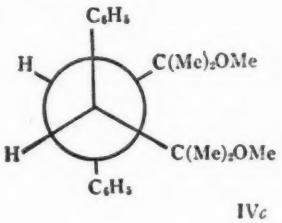
I II III

with which this *dd,ll*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (IV) may be converted to the tetrahydrofuran might have been predicted by consideration of the hindrance which would be imposed by the bulky sub-

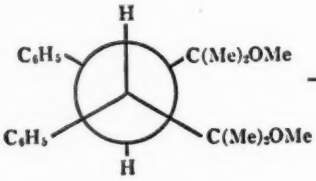
[1]*Manuscript received February 24, 1954.*
Contribution from Department of Chemistry, University of Toronto, Toronto, Ont.



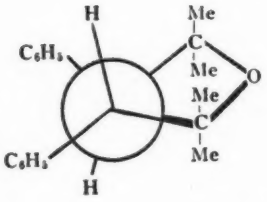
IV*b*



IV*c*

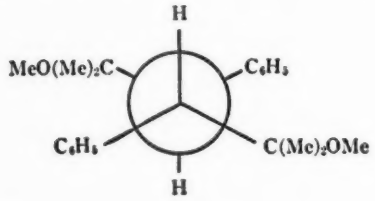


IV*a*

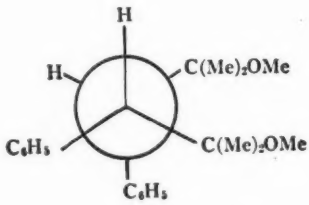


dd,ll-III

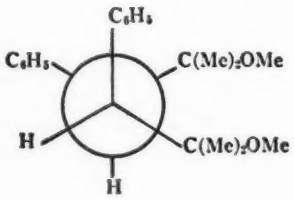
stituents. Thus of the three possible rotamers*, IV*a*, *b*, *c*, that one (IV*a*) which might be expected to be in preponderance because of symmetrical disposition and minimum in crowding of the substituent group is also the rotamer in which pivotal rotation to form *dd,ll*-III would separate the phenyl groups (compare IV*a* with *dd,ll*-III).



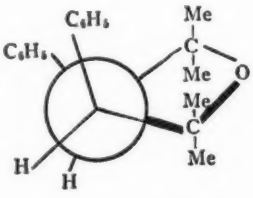
V*b*



V*c*



V*a*



meso-III

**The term "rotamer" (7) seems to us so much more appropriate than "restriction isomer" (11) that we have abandoned the latter term in favor of the former. However the concept of electrostriction is implicit in any discussion of these isomers.*

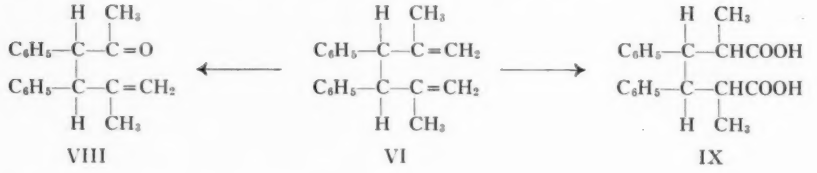
The solid 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (V) must necessarily be the *dl,ld* (*meso*) diastereomer. If one examines the structures corresponding to rotamers it is evident that the most symmetrical form (V*b*, which probably represents all of this diastereomer in the solid form) will have the conformation least favorable for cyclization to the diastereomeric 2,2,5,5-tetramethyl-3,4-diphenyltetrahydrofuran (*meso*-III). Furthermore conversion of either of the enantiomeric forms (V*a* or V*c*) to *meso*-III would be hindered to the extent that pivotal rotation would bring the phenyl groups closer together. In consequence it might be expected that this cyclization would occur with difficulty; this is found to be the fact. However the cyclization does occur under the unique influence of hydriodic acid in boiling dioxane. The product is evidently *meso*-III since it contains neither hydroxyl groups nor aliphatic unsaturation and its ultraviolet absorption spectrum is almost identical with that of *dd,ll*-III.

This method for preparation of *meso*-III is better than mixtures of hydrobromic and acetic acids which were used by Berman *et al.* (1) to obtain the same compound to which they did not assign a structure. But it should be noted that one of these two methods is required for the formation of *meso*-2,5-dimethyl-3,4-diphenyltetrahydrofuran (III), in contrast to formation of the *dd,ll* diastereomer which occurs in diverse reaction media.

In further contrast the formation of the *meso* (but not the *dd,ll*) diastereomer III is accompanied by at least one by-product. The isolable contaminant is 2,5-dimethyl-3,4-diphenylhexadiene-1,5 (VI), the preparation of which has previously been described (1) as the treatment of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (V) with sodium chloride, acetic anhydride, and sulphuric acid.

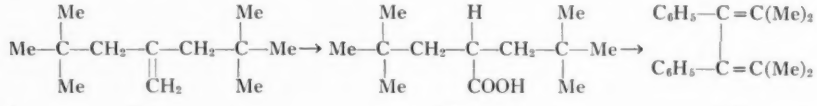
We have reinvestigated the diene VI and have improved its mode of preparation by use only of potassium bisulphate and acetic anhydride. We have also confirmed the structure of VI by ozonolysis and by catalytic reduction (with difficulty) to *meso*-2,5-dimethyl-3,4-diphenylhexane (VII) (8). This additional proof has been welcome. One might normally expect that the elimination of two molecules of methanol from V would lead to 2,5-dimethyl-3,4-diphenylhexadiene-2,4 (XII) instead of the nonconjugated 1,5-diene (VI) which actually is obtained. But such an expectation does not take into account the steric aspects of the diene XII.

However our oxidation of the isolated diene VI may explain why the conjugated diene was not obtained by demethanolation. With chromium trioxide in acetic acid four products have been isolated besides unchanged VI. In addition to benzoic acid, two diastereomeric acids have been isolated as their esters, which conform in analysis with that expected for dimethyl *ddld,lldl*- and *ddll,lldd*-2,5-dimethyl-3,4-diphenyladipates. Finally a ketone has been isolated in small amount as its dinitrophenylhydrazone; according to analysis this is 5-methyl-3,4-diphenylhexen-5-one-2 (VIII). One might expect this partial oxidation product of an ordinary nonconjugated diene. The dimethyldiphenyladipic acids (IX) are unexpected except as one considers the unusual oxidations of hindered alkenes such as 1,1-dineopentylethene (X) (4, 10). This



VIII VI IX

compound yields dineopentyl acetic acid (XI) which, like IX, contains the same number of carbon atoms as does the alkene. In view of similar evidence of hindrance in our derivatives of diphenylethane it may not be surprising that



X XI XII

no method of methanol removal from the 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexanes (IV and V) has yet produced the conjugated diene XII.

The practical preparation of 2,5-dimethyl-3,4-diphenylhexadiene-1,5 (VI) by potassium bisulphate and acetic anhydride does produce, in trace yield, another hydrocarbon of the same empirical formula, but it is not XII. Instead we believe it to be 1,1-dimethyl-3-isopropenyl-2-phenylindane (XIII) which may be prepared more satisfactorily by a two-step reaction. When *meso*-dimethoxydimethyldiphenylhexane (V) is treated with the Lucas reagent (equimolar mixture of zinc chloride and concentrated hydrochloric acid) two moles of methanol are eliminated and one mole of hydrogen chloride is added. We believe the product to be 2-chloro-2-[3,3-dimethyl-2-phenylindanyl]-propane, XIV. Treatment of XIV with alcoholic sodium hydroxide or alumina leads to the dimethylisopropenylphenylindane (XIII).

The empirical formula of XIII is established as $C_{20}H_{22}$ by elemental analysis and molecular weight determinations. The presence of the terminal double bond has been established by ozonolysis, from which a 35% yield of the dimedone derivative of formaldehyde may be isolated. This yield, under the conditions of the entire ozonolysis procedure, indicates one double bond per $C_{20}H_{22}$ unit (9). Moreover indirect proof establishing the presence of the phenylindane nucleus is afforded by examination of a second product obtained during preparation of the tertiary chloride, XIV.

Actually this second product is the major one (40 versus 17%) and like XIII, has the empirical formula $C_{20}H_{22}$. This product, 3,3-dimethyl-2-phenyl-1-isopropylindene (XV) may also be formed from *meso*-dimethoxydimethyldiphenylhexane (V) by reflux with 50% hydriodic acid (76%) or by boron fluoride etherate in boiling petroleum ether (60%) or by 90% sulphuric acid at room temperature (50% yield). This compound has been assigned structure XV for several reasons. Firstly it resists hydrogenation at 20–50° with either platinum or nickel up to 1500 lb. gauge pressure and bromine will not add to it, although substitution seems to occur. Secondly the compound behaves as

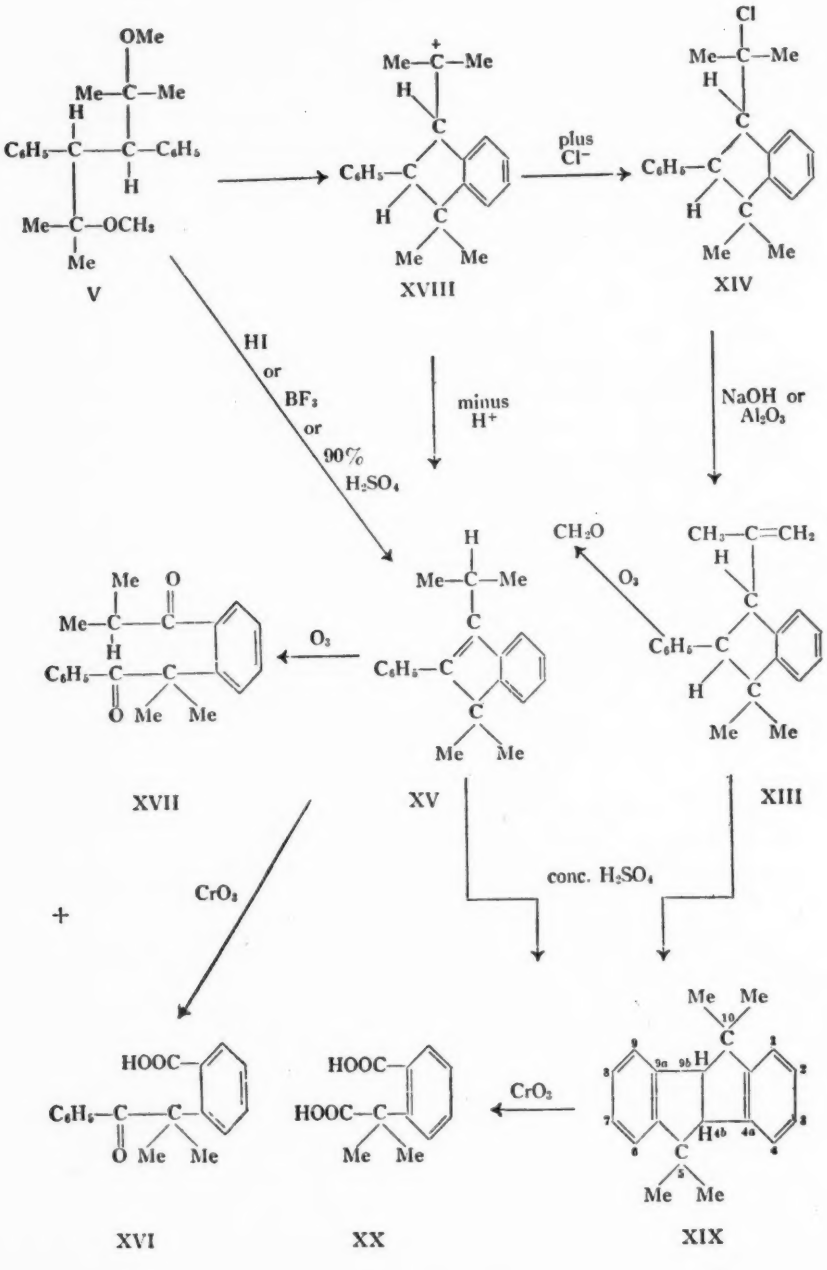
a highly-conjugated aromatic system: it imparts a deep red color to tetranitromethane, and its ultraviolet absorption resembles that of stilbene. In conformity with this similarity it reacts with sodium to form a highly-colored adduct in 1,2-dimethoxyethane (3).

The substance believed to be 3,3-dimethyl-1-isopropyl-2-phenylindene (XV) does undergo ozonization, but none of formaldehyde, acetaldehyde, or acetone can be detected among the products. However a diketone, $C_{20}H_{22}O_2$, has been isolated as its mono 2,4-dinitrophenylhydrazone. Since no carbon atoms are lost the keto linkages are evidently the result of oxidative fission of the indene double bond. In addition to this diketone the ozonization yields an acid believed to be *o*-carboxyphenylisopropiophenone (XVI) on the basis of analysis and neutralization equivalent. The keto group in this acid is nonreactive, and this property might be expected if XVI existed in ketol form. If this acid is considered to be an oxidative degradation product of the diketone then the latter may be formulated as *o*-isobutyrylphenylisopropiophenone (XVII).

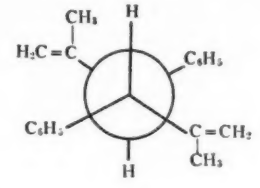
We believe that this evidence justifies the formulation of 3,3-dimethyl-1-isopropyl-2-phenylindene (XV). Since this structure is isomeric with that of 3,3-dimethyl-1-isopropenyl-2-phenylindane (XIII) the characterization of XV would tend to support that of XIII. Thus the formation of XV and (via XIV) of XIII may be presumed to proceed through an intermediate portrayed for convenience as the electropositive particle XVIII. The reaction resembles that by which 1,1-dimethyl-3-phenyl-1-propanol is converted to 1,1-dimethylindane (2) by means of 85% sulphuric acid.

According to this postulation the Friedel-Crafts type of cyclization which produces XIII and XV ought to continue further through the intermediate cation XVIII (under conditions wherein it was sufficiently stable) to form 5,5,10,10-tetramethyl-4*b*,5,9*b*,10-tetrahydroindeno[2,1-*a*]indene (XIX). Actually a compound conforming with this analysis and molecular weight may be formed by treatment of either XIII or XV or even V with concentrated sulphuric acid. However the tetracyclic XIX can best be prepared by treatment of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (V) with anhydrous hydrofluoric acid. We believe the tetracyclic structure XIX to be authentic because no reaction occurs with ozone, because the ultraviolet absorption spectrum closely resembles that of XIII and of indane itself, and finally because chromic acid oxidation gives the known α,α-dimethylhomophthalic acid, XX.

Earlier in this report it has been suggested that bulky substituents on the central carbon atoms in diphenylethane tend to cause restriction about the pivotal linkage. According to this postulation the most stable (symmetrical) form of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane, V*b*, would form the cyclic ether, *meso*-2,5-dimethyl-3,4-diphenyltetrahydrofuran (*meso*-III), with difficulty in contrast to the easy conversion of IV to *dd*,*ll*-III. On the other hand inspection of structure V*b* shows that this spatial conformation is favorable to removal of methanol by a Friedel-Crafts mechanism via intermediates which (for purposes of illustration) may be represented by the dication XXI. Loss of two protons may thus lead with conformational con-

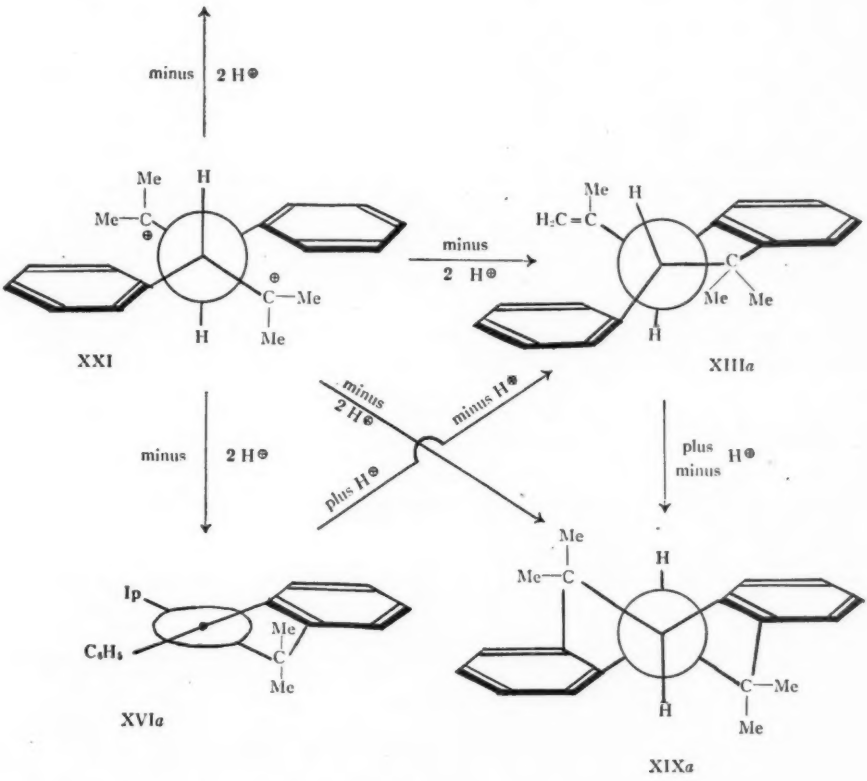

OMe
Me—C—Me
H
C6H5—C—C—C6H5
H
Me—C—OCH3
Me
V
Me—C—Me
H
C
C6H5—C
H
C
Me Me
XVIII
plus Cl⁻
Cl
Me—C—Me
H
C
C6H5—C
H
C
Me Me
XIV
HI or BF3 or 90% H2SO4
minus H+
NaOH or Al2O3
H
Me—C—Me
C
C6H5—C
C
Me Me
XV
CH2O
O3
CH3—C=CH2
H
C
C6H5—C
H
C
Me Me
XIII
Me O
Me—C—C
H
C6H5—C—C
O Me Me
XVII
O3
conc. H2SO4
CrO3
+
HOOC—
C6H5—C—C
O Me Me
XVI
HOOC—
HOOC—C
Me Me
XX
CrO3
Me Me
10
C
9
1
8
2
9a 9b H
7
3
H 4b 4a
6
4
C
5
Me Me
XIX

venience to the indane, XIII*a*, or the indene, XVI*a* (the latter being convertible by proton exchange to the former), while the same convenience may lead directly by proton loss from XXI to the indeno-indene (XIX*a*), also by proton exchange from XIII*a*. These Friedel-Crafts processes do not preclude



VI*a*

XII*a*



direct proton loss from XXI to the nonconjugated diene VI*a*, but it may be seen that steric hindrance prevents the coplanarity expected for conjugation in the formation of XII*a*. The series of products arising from methanol fission from *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (*meso*-III)

thus are expected ones from the aspect of steric restriction. However the specificity in respect of which the several products are formed in different reaction media shows that free-cationic structures such as XXI are probably fallacious and are certainly inadequate from the aspect of prediction. Such prediction may become possible when more is known about the co-ordination complexes of which free-ionic structures such as XXI represent a simplification.

EXPERIMENTAL*

meso-2,2,5,5-Tetramethyl-3,4-diphenyltetrahydrofuran (meso-III)

A solution of 0.5 gm. (0.00153 mole) of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane, m.p. 137–138° C., and 0.30 ml. (0.0017 mole) of hydriodic acid (density 1.57) in 7.5 ml. of dioxane was boiled under reflux for eight hours, then poured into ice and the solid, m.p. 70–78° C. (0.37 gm., 86%), was filtered off. This crude product was extracted with 0.5 ml. of 95% ethanol leaving 2 mgm., m.p. 159–163° C., of 2,5-dimethyl-3,4-diphenylhexadiene-1,5 (VI). Evaporation of the extract left a residue, m.p. 84–87° C., which was heated at 80° C. (10 mm.) for two days. The residue, after this sublimation of impurities, weighed 0.23 gm. (53%), m.p. 92–93° C. This compound showed neither addition nor active hydrogen in the Grignard machine and it contained no methoxyl function. The ultraviolet absorption spectrum comprised a single peak at 260 mμ with $E_{molar} = 350$. The spectrum resembled closely that of the *dd,ll* diastereomer ($E_{molar} = 325$), except that absorption was slightly greater throughout the curve.

2,5-Dimethyl-3,4-diphenylhexadiene-1,5 (VI)

A solution of 5.0 gm. (0.0153 mole) of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (*meso*-III) and 2.1 gm. (0.0154 mole) of anhydrous po-

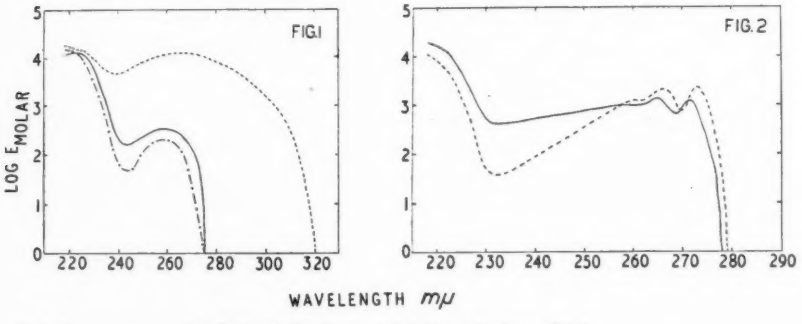


FIG. 1. – – – – – – 3,3-Dimethyl-1-isopropyl-2-phenylindene (XV)
———— *meso*-2,5-Dimethyl-2,5-dimethoxy-3,4-diphenylhexane (V)
— · — · — 2,5-Dimethyl-3,4-diphenylhexadiene-1,5 (VI)
FIG. 2. – – – – – – 5,5,10,10–Tetramethyl-4*b*,5,9*b*,10-tetrahydroindeno[2,1-*a*]indene (XIX)
———— 1,1-Dimethyl-3-isopropenyl-2-phenylindane (XIII)

**Melting points have been corrected against reliable standards. X-ray diffraction patterns are recorded as relative intensities [I/I_1] at d spacings in Å using CuK_α radiation (Ni filtered). Only the strongest lines were recorded.*

tassium bisulphate in 50 ml. of acetic anhydride was boiled under reflux for four hours, then diluted with ice. The crude precipitate was water-washed, 3.15 gm., m.p. 90–143° C. It was dissolved in 30 ml. of hot absolute ethanol, filtered, and cooled, yielding 1.24 gm. (31%) of VI, m.p. 161–163° C. A mixture melting point with the substance reported previously (1) was not lowered. The ultraviolet absorption spectrum is shown in Fig. 1 for an ethanolic solution (4.21×10^{-5} moles per liter).

The ethanolic mother liquors were evaporated and the residue, m.p. 67–93° C., was sublimed at 65° C. (8 mm.), yielding 91 mgm., m.p. 71–74° C. (2%), of impure 1,1-dimethyl-3-isopropenyl-2-phenylindane (XIII).

Oxidation of meso-2,5-Dimethyl-3,4-diphenylhexadiene-1,5 (VI)

A mixture of VI (1.25 gm., 0.0048 mole) and 1.87 gm. (0.0187 mole) of dichromium trioxide, 50 ml. of acetic acid and 1.5 ml. (0.0833 mole) of water was heated at 90–100° C. with stirring for one hour, then diluted with 50 ml. of water. The insoluble phase was filtered and dissolved in 10 ml. of diethyl ether plus 10 ml. of 5% aqueous sodium hydroxide. The etherous phase, washed with water, then dried and evaporated, left 97 mgm., m.p. 137–152° C. Crystallization from 1 ml. of absolute ethanol left 53 mgm. (4%) of unchanged VI, m.p. 159–162° C. The alkaline phase was acidified with concentrated hydrochloric acid. The precipitate, 0.207 gm. (13%), m.p. 305–308° C., was crystallized from acetic acid (120 ml. per gm.), m.p. 325–326° C. Strongest lines of the X-ray powder diagram are: [10] 4.21, 4.00; [7] 5.71, 4.69, 4.48, 3.83. Neut. equiv. calc. for $C_{20}H_{22}O_4$, 163; found, 155. This diastereomer of 2,5-dimethyl-3,4-diphenyladipic acid (IX) was converted by etherous diazomethane into the methyl ester, crystallized from methanol, 100 ml. per gm., m.p. 108–109° C. Calc. for $C_{22}H_{26}O_4$: C, 74.5; H, 7.39. Found: C, 74.8; H, 7.41.

The original drowned reaction system from which VI and one diastereomer of IX had been removed by filtration was twice-extracted with 25-ml. portions of ether. This ether was water-washed and then thrice-extracted with 5-ml. portions of 5% aqueous alkali. The etherous phase was then evaporated leaving 0.372 gm. of an oil, 50 mgm. of which was treated with 1 ml. of a methanolic solution of 2,4-dinitrophenylhydrazine containing hydrogen chloride. The dinitrophenylhydrazone of 5-methyl-3,4-diphenylhexen-5-one-2 (VIII) (30 mgm., m.p. 211–214° C.) was twice-crystallized from 1:1 ethanol – ethyl acetate (0.16 ml. per mgm.), m.p. 230–230.5° C. Calc. for $C_{25}H_{24}N_4O_4$: C, 67.6; H, 5.44; N, 12.6. Found: C, 68.2; H, 5.36; N, 12.4.

The combined alkaline extract of the etherous solution of VIII was acidified with concentrated hydrochloric acid. The gummy precipitate (0.475 gm.) was removed. The remaining aqueous phase, by ether extraction and sublimation after evaporation of the ether, yielded 11 mgm. (2%) of benzoic acid. The gummy precipitate was boiled under reflux with 2 ml. of methanol containing 10 mgm. of 96% sulphuric acid for three hours, then cooled to 0° C. This crude second diastereomer of dimethyl 2,5-dimethyl-3,4-diphenyladipate (ester of IX), 25 mgm., m.p. 130–140° C., was four times crystallized from 0.5 ml. of

methanol, m.p. 163–164.5° C. Calc. for $C_{22}H_{26}O_4$: C, 74.5; H, 7.39. Found: C, 74.1; H, 7.45.

meso-2,5-Dimethyl-3,4-diphenylhexane (*VII*)

A solution of 80 mgm. (0.000306 mole) of 2,5-dimethyl-3,4-diphenylhexadiene-1,5 in 10 ml. of absolute ethanol containing 1 gm. of Raney nickel catalyst (W-1) was shaken 19 hr. with hydrogen at 1500 lb. pressure. The system was filtered and evaporated, leaving 63 mgm. (79%) of *meso*-dimethyldiphenylhexane, m.p. 149–150.5°. A mixture melting point with authentic material (7) was not depressed.

dl,ld-2-Chloro-2-[3,3-dimethyl-2-phenylindanyl]-propane (*XIV*)

A system comprising 1.00 gm. (0.00306 mole) of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (*meso*-III) and 4.1 gm. (0.03 mole) of zinc chloride in 2.5 ml. (0.03 mole) of concentrated hydrochloric acid was stirred for 12 hr. The oily solid was taken up in 15 ml. of petroleum ether (b.p. 40–60° C.); the solution was washed thoroughly with water, then dried, and evaporated. The crude 3,3-dimethyl-1-isopropyl-2-phenylindene (XV, 0.861 gm.) was crystallized from 5 ml. of hot methanol, 0.322 gm. (40%), m.p. 67–68° C. A mixture melting point with the compound described later in this report was not depressed.

The methanolic filtrate was diluted to a volume of 10 ml., chilled to −80°C., and filtered to separate 0.16 gm. (18%) of the crude chloro compound XIV, m.p. 78–83° C. After two recrystallizations it melted at 89–90.5° C. and still gave a positive halide test with alcoholic silver nitrate. Calc. for $C_{20}H_{23}Cl$: C, 80.4; H, 7.76. Found: C, 79.7; H, 7.85.

3,3-Dimethyl-1-isopropenyl-2-phenylindane (*XIII*)

A. From XIV with Alcoholic Alkali

A solution of 0.23 gm. (0.01 atom) of metallic sodium in 3 ml. of absolute ethanol was combined with 0.076 gm. (0.000255 mole) of XIV in 1 ml. of the same solvent and boiled for two hours under reflux, then cooled, and diluted with 50 ml. of water. After slow separation the crude dimethylisopropenylphenylindane (XIII), 66 mgm. (99%), m.p. 67–73° C., was crystallized from hot methanol (1 ml. per gm.), m.p. 76–77° C. Mol. wt. (Rast) was calculated as 262; found 258. The X-ray powder pattern was: [10] 5.40, 5.18; [5] 3.80; [4] 6.32, 4.46, 4.07, 3.66. Calc. for $C_{20}H_{22}$: C, 91.5; H, 8.45. Found: C, 91.7; H, 8.61.

B. From XIV with Alumina

The crude reaction product from the preparation of XIV described above (0.837 gm.) was dissolved in 5 ml. of petroleum ether (b.p. 40–60° C.). This solution, on a 1.5 × 45 cm. column of alumina, was eluted with the same solvent yielding 0.486 gm. (61%) (75 ml. eluent) of 3,3-dimethyl-1-isopropyl-2-phenylindene (XV, m.p. 67–69° C.), 0.080 gm. (25 ml. eluent) of intermediate fraction, m.p. 50–65° C., and 0.242 gm. (30%) (100 ml. eluent) of 3,3-dimethyl-1-isopropenyl-2-phenylindane (XIII, m.p. 73–75° C.). The ultraviolet absorption spectrum of XIII is shown in Fig. 2.

Ozonization of 3,3-Dimethyl-1-isopropenyl-2-phenylindane (XIII)

A solution of 0.102 gm. (3.88×10^{-4} mole) of XIII in 6 ml. of pre-ozonized and purified carbon tetrachloride was treated with 1.8 liters of 6% ozonized oxygen at 0° during 100 min. The solid ozonide was hydrolyzed with 20% acetic acid and 150 mgm. of zinc dust in the carbon tetrachloride medium at 40–50° C. with a stream of nitrogen bubbling through. No acetone could be detected in the effluent gas by acid-methanolic 2,4-dinitrophenylhydrazine. The nonaqueous layer was removed.

The aqueous layer was distilled almost completely and the distillate adjusted to pH 4.0–4.5 with acetic acid and sodium hydroxide; then 0.1 gm. of dimedone in 30 ml. of water was added. The precipitate, methylene-*bis*-dimethyldihydroresorcinol, weighed 0.386 gm., m.p. 188–189° C., mixture melting point with authentic material not lowered. Yield of formaldehyde is thus 34.6% based on one methylene group per mole of XIII.

3,3-Dimethyl-1-isopropyl-2-phenylindene (*XV*)

A system comprising 5.0 gm. (0.0153 mole) of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (*meso*-III) and 70 ml. of hydriodic acid (density 1.54) was boiled under reflux for 12 hr., then poured into ice. The crude product, 4.12 gm., m.p. 55–62° C., was dissolved in 10 ml. of hot methanol and the solution was cooled to 0° C. The crystals, 3.06 gm. (76%), m.p. 68.5–69.5° C., were recrystallized from hot methanol (2 ml. per gm.), m.p. 69–70° C. Calc. for $C_{20}H_{22}$: C, 91.5; H, 8.45. Found: C, 91.3; H, 8.65.

The X-ray powder pattern of XV is: [10] 4.19; [9] 4.72; [8] 7.49, 6.96, 6.15, 5.71. The ultraviolet absorption spectrum in absolute ethanol (4.32×10^{-5} moles per liter) is shown in Fig. 1. *meso*-III may also be converted to XV in 50% yield by 90% sulphuric acid at 25° C. or in 60% yield by boron fluoride etherate in boiling petroleum ether (b.p. 40–60° C.).

Disodium Adduct of XV

A solution of 0.26 gm. (0.001 mole) of dimethylisopropylphenylindene (XV) in 7 ml. of 1,2-dimethoxyethane was shaken with 0.10 gm. (0.0041 atom) of sodium under nitrogen. A deep red color appeared at once. After three days the system was treated with gaseous carbon dioxide; then the dimethoxyethane was vacuum-evaporated and replaced with 10 ml. each of diethyl ether and water. The etherous phase, water-washed, dried, and evaporated left 0.13 gm. (50%) of an oily solid which, crystallized from 2 ml. of methanol, gave 50 mgm. (19%) of unchanged XV.

The alkaline phase was acidified with concentrated hydrochloric acid to precipitate 0.13 gm., m.p. 156–175° C. From this mixture was isolated a few milligrams of pure compound by crystallization from 85: 15 petroleum ether (b.p. 60–70° C.) – benzene (30 ml. per gm.), m.p. 203–204° C. Calc. for $C_{21}H_{24}O_2$: C, 81.7; H, 7.85. Found: C, 81.8; H, 8.04. According to this analysis the compound is 3,3-dimethyl-1-isopropyl-2-phenyl-1 or 2-indanecarboxylic acid. However if the hydrogen value were slightly in error the compound could be 3,3,3′,3′-tetramethyl-1,1′-diisopropyl-2,2′-diphenylbiindanyldicarboxylic acid.

Ozonization of XV

A solution of 1.04 gm. (0.004 mole) of XV in 25 ml. of preozonized and purified carbon tetrachloride was treated with 4.1 liters of 5% ozonized oxygen during three hours. The solvent was vacuum-evaporated and the residual oily ozonide was hydrolyzed by heating it under reflux with 15 ml. of water, 300 mgm. of zinc dust, and 1 mgm. each of hydroquinone and silver nitrate. The mixture was filtered, the zinc was washed with 15 ml. of benzene, and the phases were separated. The aqueous phase was warmed to 40–50° and a stream of nitrogen was bubbled through it. No acetone in the effluent could be detected by dinitrophenylhydrazine reagent. The aqueous layer was then distilled, but dimedone showed the absence of any formaldehyde in the distillate.

The benzene phase was extracted once with 10 ml. of 10% aqueous sodium hydroxide and twice with 5-ml. portions of water. The combined extracts were acidified with concentrated hydrochloric acid, precipitating 0.130 gm., m.p. 173–190° C. This crude *o*-carboxyphenylisopropiophenone (XVI) was crystallized from 2 ml. of benzene, 0.115 gm. (11%), m.p. 208.5–209.5° C. Potentiometric titration showed $K_A = 4.5 \times 10^{-7}$. Calc. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.01; neut. equiv., 268. Found: C, 75.8; H, 6.04; neut. equiv., 256. The mother liquor from the crystallization yielded 1% of benzoic acid.

The benzene phase from which XVI was alkali-extracted was dried and then evaporated. When the oily residue (0.956 gm.) was treated with excess acid-methanolic 2,4-dinitrophenylhydrazine a derivative (0.446 gm.) was obtained, m.p. 201–203° C. This dinitrophenylhydrazone of *o*-isobutyrophenylisopropiophenone (XVII) was crystallized from acetic acid (20 ml. per gm.), m.p. 206–207° C. Calc. for $C_{26}H_{26}N_4O_5$: C, 65.8; H, 5.52; N, 11.8. Found: C, 65.3; H, 5.51; N, 11.9.

When the ozonide of XV was heated in water alone (oxidative hydrolysis) a 28% yield of benzoic acid and a 13% yield of XVI was isolated, but none of the carbonyl-containing XVII was found. If, instead of ozonization, XV was oxidized with sodium dichromate – sulphuric acid in acetic acid the only isolable product was XVI.

5,5,10,10-Tetramethyl-4b,5,9b,10-tetrahydroindeno[2,1-a]indene (XIX)

A. From meso-III and Concentrated Sulphuric Acid

The *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (*meso*-III, 0.50 gm., 0.00153 mole) was added to 5.0 ml. of concentrated sulphuric acid at 25° C. A bright red color appeared and an oil separated which crystallized after seven hours. The system was drowned with ice and the crude solid (88 mgm., 22%, m.p. 78–79° C.) was crystallized from 0.5 ml. of hot methanol, 51 mgm. of XIX, m.p. 82–83° C. Variation in time, temperature, or amount of sulphuric acid did not alter the yield. Calc. for $C_{20}H_{22}$: C, 91.5; H, 8.45; Mol. wt. (Rast), 262. Found: C, 91.5; H, 8.62; mol. wt. (Rast), 270.

B. From meso-III and Hydrogen Fluoride

The *meso*-III (2.50 gm., 0.077 mole) was added to 160 gm. of liquid hydrogen fluoride at −80° C. in a polythene bottle. A bright orange color developed.

The mixture was stirred for three to five hours at 0° C. and then was poured into ice. The aqueous mixture was extracted with 100 ml. of diethyl ether. This extract was washed with 10% aqueous alkali, then with water, and dried. The residue left by ether evaporation (1.93 gm., m.p. 70–77° C.) was crystallized from 7 ml. of hot methanol, 1.47 gm. (73%), m.p. 82–83° C. No reduction was apparent when the product was boiled for three hours with an excess of sodium in ethanol. XIX was also recovered after treatment with ozone. The ultraviolet absorption spectrum of XIX, Fig. 2, resembles that of indane when determined in absolute ethanol (5.30×10^{-5} moles per liter).

C. From Dimethylisopropenylphenylindane (XIII) and Sulphuric Acid

When 31.1 mgm. (1.19×10^{-5} mole) of XIII was added to 3.0 ml. of 96% sulphuric acid at 0° C. it liquefied and a yellow color appeared. After six hours the oil solidified. The solid obtained after drowning with ice weighed 10.6 mgm. (34%), m.p. 81–82° C., mixture melting point with material from *A* and *B* not lowered.

D. From Dimethylisopropylphenylindene (XV) and Sulphuric Acid

The hydrocarbon (XV, 10 mgm., 3.9×10^{-3} mole) was added to 0.10 ml. of 96% sulphuric acid at 20° C. A yellow color appeared but the solid did not liquefy rapidly. After five hours ice was added and the solid filtered, 2 mgm., m.p. 79–80° C. A mixture melting point with material prepared according to *A*, *B*, or *C* was not lowered. The product was recovered: 99% after one day at 15 lb. hydrogen pressure with Adams' platinum catalyst, 75% after shaking with Raney nickel catalyst (W-2) at 1500 lb. hydrogen pressure either at 25° C., 55° C., or 80° C.

Bromination of Tetramethyltetrahydroindenoindene (XIX)

A solution of 0.52 gm. (0.002 mole) of XIX in 20 ml. of carbon tetrachloride with 0.64 gm. (0.008 mole) of bromine became colorless after eight hours and 0.64 gm. (0.0051 mole) of hydrogen bromide was evolved. Evaporation of the system left 0.801 gm. which was crystallized from benzene (20 ml. per gm.) finally to melt at 313–314° C. Elemental analysis showed the compound to contain bromine although it would not react with alcoholic silver nitrate. The X-ray diffraction powder diagram was: [10] 5.68, 5.52; [9] 3.33; [6] 6.25, 6.00, 3.85, 3.75. Calc. for $C_{20}H_{18}Br_2$: C, 57.4; H, 4.34. Found: C, 58.0; H, 4.46.

The first mother liquor from the benzene crystallization was evaporated and treated to get a steam distillate, 0.22 gm., m.p. 75–105° C. Repeated crystallization from petroleum ether (b.p. 60–70° C., 15 ml. per gm.) and from absolute ethanol (15 ml. per gm.) left 10 mgm., m.p. 206–207° C. Calc. for $C_{20}H_{19}Br$: C, 70.8; H, 5.64. Found: C, 70.7; H, 5.78.

Oxidation of Tetramethyltetrahydroindenoindene (XIX)

Either hot aqueous nitric acid or potassium permanganate seems to be inadequate as an oxidizing agent for XIX, but chromic acid is effective. A mixture of 12.0 gm. (0.04 mole) of sodium dichromate dihydrate in 43 ml. of 50 volume per cent aqueous sulphuric acid and 30 ml. of acetic acid was stirred for 20 hr. with 2.08 gm. (0.008 mole) of XIX.

The system was then diluted with 50 ml. of water and extracted with 70 and then 20 ml. of diethyl ether. The etherous phase was washed with water, then extracted with alkali followed by water. The etherous phase was then dried and evaporated, leaving 1.05 gm. of gum which was crystallized from 5 ml. of hot absolute ethanol, 0.32 gm. (13%), m.p. 203–205° C. (after recrystallization, 205–205.5° C.). Calc. for $C_{20}H_{20}O_3$: C, 77.9; H, 6.53. Found: C, 78.3; H, 6.65. This product of unknown structure was recovered unchanged after long heating with hot 15% alkali in which it was insoluble. It reacted neither with hot hydrogen bromide in acetic acid nor with hydrogen in presence of Adams' platinum catalyst. It was also inert toward chromic acid and permanganate (in acetone) oxidation.

Evaporation of the mother liquor from the ethanolic crystallization of the 1.05 gm. of gum left a residue, m.p. 60–70° C., which was extracted with 10 ml. of hot petroleum ether (b.p. 40–60° C.). When cool the insoluble portion (0.288 gm.) melted at 180–206° C. while the solution, evaporated, left 0.508 gm., m.p. 65–75° C. The latter was crystallized from 2 ml. of hot methanol, 0.354 gm. (17%) of unchanged XIX, m.p. 82–83.5° C., mixture melting point not depressed. The 0.288 gm. portion was crystallized from 2 ml. of benzene, 0.035 gm., m.p. 236–240° C. For analysis this was crystallized from 1 ml. of methanol, m.p. 237–238.5° C. Calc. for $C_{20}H_{22}O_3$: C, 77.4; H, 7.14. Found: C, 77.4; H, 7.26.

The alkaline extract of the original ether solution was acidified with concentrated hydrochloric acid and then extracted with diethyl ether. This extract, dried, was evaporated, leaving 0.16 gm. which was sublimed at 100° C. (8 mm.) for 40 hr. The sublimate, 0.0983 gm., m.p. 65–72° C., was fractionally resublimed at 80° C. (10 mm.) to obtain an intermediate fraction, 52 mgm. (3%), m.p. 75–78° C. Crystallization of this crude dimethylhomophthalic anhydride from petroleum ether (b.p. 40–60° C., 10 ml. per gm.) raised the melting point to 80–81° C. Calc. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.30. Found: C, 69.5; H, 5.30. This anhydride (5 mgm.) was dissolved in 0.5 ml. of 3% aqueous sodium hydroxide, then acidified with 0.05 ml. of concentrated hydrochloric acid, yielding the dimethylhomophthalic acid (XX, m.p. 126–127.5° C.). Vacuum resublimation converted XX to the anhydride. The alkaline solution of the anhydride was potentiometrically titrated with hydrochloric acid, equivalent weight, 94.6 (calc., 95.1), approximately $K_{A_1} = 2.5 \times 10^{-4}$, $K_{A_2} = 5.6 \times 10^{-6}$. When the anhydride (5 mgm.) was dissolved in 1 ml. of 10% aqua ammonia and the solution was evaporated to dryness, either the acid-amide or the diamide must have been formed (m.p. 165–173° C.); it was sublimed at 200° C. (8 mm.), m.p. 105–109° C. This crude homophthalimide, after two crystallizations from 0.25 ml. of water, melted at 118–119° C. The melting point reported previously (5, 6) is 119–120° C.

When the ratio of XIX to oxidizing agent was decreased the amount of $C_{20}H_{20}O_3$ was increased to 14% while none of the dimethylhomophthalic anhydride could be isolated. In contrast, increase of the ratio increased the yield of the anhydride to 7%.

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DIELECTRIC RELAXATION IN CELLULOSE CONTAINING SORBED VAPORS[1]

By R. Seidman[2] and S. G. Mason

ABSTRACT

The dielectric constant and dielectric loss factor were measured in a dispersion region for a paper of high cellulose content. The complex arrangement of the paper in the measuring condenser did not effectively alter the position of the dispersion region of the paper itself, as shown by electrical analysis. From this analysis equations were derived from which the dielectric constant and maximum dielectric loss factor of the cellulose fiber were evaluated for varying amounts of sorbed water, methanol, and ethanol. The effect of each of these vapors on the position of the dispersion region was studied, measurements being performed over a range of frequency of 10 to 1000 kc.p.s., and a range of temperature of −58 to 26°C. A typical plasticizing action was observed in all three cases. This was confirmed from an analysis of the data using the theory of absolute reaction rates.

INTRODUCTION

The effect of sorbed vapors of polar compounds, particularly water, on various properties of cellulose has been extensively investigated. This communication describes a study of the influence of sorbed water, methanol, and ethanol on the dielectric properties. By analogy with other polymer systems, it was considered that the pronounced swelling action of these vapors would be reflected by definite changes in the dielectric relaxation times and related properties.

It is convenient to characterize the effective dielectric constant ϵ in terms of its vector components by the relation:

$$\epsilon = \epsilon' - i\epsilon''$$

where ϵ' is the usual dielectric constant and ϵ'' is the loss factor. The angular frequency ω_{max} at which ϵ'' at a given temperature is at a maximum may be used to define a temperature-dependent relaxation time T defined by:

$$\mathrm{T} = \frac{1}{\omega_{max}}$$

a measure of the ease of oscillation of the dipoles involved. This may be measured as well by the temperature T_m at which ϵ'' at a given frequency is at a maximum.

In general, log T is an approximately linear function of the reciprocal of the absolute temperature. This suggests an energy term which Eyring (16) expresses in the form:

$$\frac{1}{\mathrm{T}} = \frac{kT}{h} e^{-\Delta F^*/RT}$$

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Contribution from the Pulp and Paper Research Institute of Canada and the Department of Chemistry, McGill University, Montreal, Quebec.
[2]*Holder of a Fellowship from the National Research Council of Canada.*

where k and h are Boltzmann's and Planck's constants, respectively, and ΔF^* is the free energy of activation for dielectric relaxation. This can be rewritten as:

$$\frac{1}{\mathrm{T}} = \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$

where ΔS^* and ΔH^* are the corresponding entropy and enthalpy for dielectric relaxation.

Investigations have been made on rubber swollen in both polar and non-polar solvents (24). From measurements at constant frequency, it was found that T_m was shifted in varying degree to lower temperatures by increases in concentration of swelling agent; at the same time there was a decrease in ΔH^*. Similar effects were produced in polyvinyl chloride by tetralin (15), diphenyl (14), and tricresyl phosphate (7), in polycaproamide by water and methanol (12), and in starch by water (20). On the other hand, the vulcanization of rubber with increasing amounts of sulphur is accompanied by regularly increasing values of ΔH^* and ΔS^* (19, 25). Stoops (26) measured the dielectric relaxation in dry cellophane. An analysis of his data shows no significant difference in the values of T whether calculated from data obtained at constant temperature or at constant frequency. There is no reason why this should not also be the case for other forms of cellulose.

Because of the softening action of water on cellulose, it was reasonable to assume that sorbed moisture facilitates dipole rotation and thus appropriately shifts the position of maximum absorption. Limited data on this effect has been reported, but the results appear to be contradictory.

Dakin and Auxier (6) measured the dielectric constant and dissipation factor of commercial papers as a function of frequency at 28°C. When observable, the frequency of maximum absorption was unaffected by the moisture content. Similar measurements by Henniger (17) at −5°C. for paper with moisture contents of 0 and 5.6% gave the same general results.

On the other hand Veith (28) measured the dissipation factor of paper at different moisture contents as a function of temperature over the range 0 to 40°C. at fixed frequencies. The temperature of maximum loss, observed only at the highest experimental frequency, 100 kc.p.s., appeared to decrease with increasing moisture content.

In view of this conflicting evidence further investigation appeared desirable. It was decided to work with a purified form of cellulose in order to eliminate effects due to high loss impurities. The working frequencies chosen were such that absorption regions appeared in the temperature range −60 to 25°C.

EXPERIMENTAL

Dielectric Cell

The cell in which the dielectric measurements were made was designed so that the amount of vapor sorbed by the cellulose could be systematically varied. It consisted of two concentric pyrex cylinders connected at a standard-taper ground-glass joint A (Fig. 1). Platinum electrodes were deposited on the

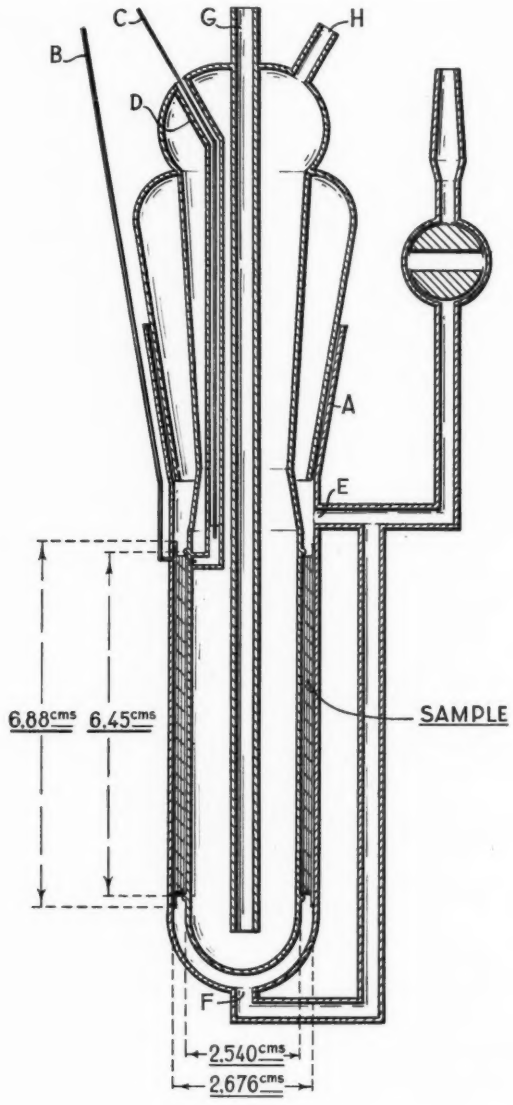


FIG. 1. Dielectric cell.

glass wall on each side of the annular space and were connected to the lead wires *B* and *C* through platinum seals. Four buttons of glass sealed both above and below the electrode on the inner cylinder served as spacers for the sample. The cell could be connected via the standard joint on the side arm to a vapor

conditioning system, access of the vapor to the sample being through E and F to both ends of the annular sample space.

The cell was calibrated with dry benzene at 25.0°C. Assuming the dielectric constant of benzene at this temperature (3) to be 2.274, the geometric capacitance, C_g, was found to be 68.0 $\mu\mu$f., while the extraneous capacitance, C_0, including leads, was 9.0 $\mu\mu$f.

The cell was connected to the measuring circuits using a system of leads having a minimum length and a fixed geometry.

Electrical Apparatus

Measurements of capacitance and equivalent a-c. conductance at 1 and 0.55 Mc.p.s. were made using a General Radio Type 821-A Twin-T Impedance measuring circuit, necessary corrections being made for residual impedances, as described elsewhere (13). A General Radio Type 716-C Schering bridge was employed for measurements at lower frequencies. D-c. resistance measurements were made with a General Radio Type 1861-A Megohmmeter; the contribution of the d-c. conductance to the a-c. loss was negligible and no correction for this effect was found necessary.

Materials

The cellulose investigated was a sample from Schleicher and Schuell No. 589 Red Ribbon quantitative filter paper having an ash content of 0.007%. Microscopic examination of the paper indicated it to be a rag furnish containing 75% linen fiber and 25% cotton. The analysis was as follows:

α-cellulose	98.4%
pentosan	1.1%
cupriethylene diamine viscosity	15.7 centipoises

Saturated aqueous solutions of potassium acetate, magnesium chloride, and potassium carbonate were used for conditioning the sample to different water contents.

Absolute ethanol and absolute methanol were dried according to the method of Lund and Bjerrum (21).

Method

The vapor content was determined on a separate sample of paper to within 0.1% using a quartz spiral mounted in a sorption cell which could be connected to the dielectric cell and/or the tube containing the vapor source, all three being maintained at 25.00 ± 0.05°C. in a water bath. In this way the paper suspended from the spiral could be subjected to the same experimental conditions of temperature and relative humidity as the paper in the dielectric cell.

Throughout this work the amount of sorbed vapor was always taken up in the direction of increasing vapor contents.

A strip of paper was tightly wrapped around the inner cylinder of the dielectric cell between the spacers and held in place by means of a spot of Glyptal cement. The cell with the paper fitting snugly into the annular space

was assembled and evacuated at 25.00 ± 0.05°C. for a period of 20 hr. Paper conditioned in this way is considered to be dry, although it is pointed out that a small quantity of water probably remained, amounting to as much as 0.4% (29, 30) which would require more drastic methods for removal (18).

A series of dielectric measurements (described below) was carried out.

The cell was then exposed to the potassium acetate solution for 48 hr. to establish equilibrium, disconnected, and dielectric measurements carried out as before. This procedure was repeated for each of the other salt solutions.

The dielectric runs were carried out at fixed frequencies. A dewar flask filled with toluene and fitted with a small variac-controlled heater served as bath for the cell. Some of the runs were performed by going up the temperature scale, others by going down, cooling being accomplished by means of dry ice. By determining a complete cycle at a single frequency, it was shown that there was no temperature hysteresis. Some slight exception to this was found in the work with methanol and ethanol, and will be described later.

With dry paper, *in vacuo*, a marked temperature hysteresis was observed. This resulted from the low thermal conductivity in the evacuated cell. The effect was eliminated by introducing a small amount of dry nitrogen gas, which served as a heat conductor.

In the experiments with methanol and ethanol it was necessary to avoid continuous exposure of the stopcocks in the conditioning system to alcohol vapors over the long periods (several weeks) necessary for a complete series of measurements with a given vapor. Furthermore, since methanol (23), and presumably ethanol, cannot be completely removed from cellulose by evacuation at room temperature, it appeared desirable to use as reference for the measurements not only the paper in a dry condition but paper containing these tightly held portions of alcohol as well. The following modifications of the above procedure were accordingly adopted.

Methanol vapor admitted to the conditioning system at a pressure of 60 mm. was allowed to remain in contact with the previously dried paper for two hours and the system was then evacuated over a second period of two hours. This process was repeated twice, the final evacuation being extended over a period of 12 hr., when the methanol content was 1.7%. After a series of dielectric measurements was performed, the paper was conditioned to a methanol content of 2.5% and a further series of dielectric measurements was made. The paper was then subjected to a further process of alternate methanol conditionings up to a methanol content of 7.0%. Before each conditioning, air was admitted to the system to permit regreasing of stopcocks, after which evacuation was carried out over a period of 12 hr., as before. With one exception, the amount of tightly bound methanol determined after the evacuation was always reproducible within experimental error.

After the experiments on methanol were completed, the residual alcohol was removed following the method of Russell, Maass, and Campbell (23). Water vapor was admitted to the system at 100% *R.H.* and was allowed to remain in contact with the paper for several hours. The system was then evacuated over a period of 15 hr., water vapor was readmitted, and the evacuation was repeated.

The net amount of sorbed vapor after this treatment was 0.2%; assuming this to be methanol 85% of the residue was therefore removed.

The paper was next conditioned to an ethanol content of 8.5% and the dielectric measurements were made. Evacuation of the system for six hours left 2.3% residual ethanol, none of which was removed after a subsequent evacuation lasting 14 hr. Dielectric measurements were performed at this ethanol content as well as at 4.6 and 6.9%. For reasons to be mentioned later these runs were all performed over a complete temperature cycle.

Two samples of paper were employed for dielectric measurements in the course of this work. Sample No. 1 was used for the work on water and No. 2 for the work on methanol and ethanol. The dimensions of the samples as well as the appropriate volume fractions are presented in Table I.

TABLE I

SAMPLE DIMENSIONS AND VOLUME FRACTIONS IN DIELECTRIC CELL

Sample No.	Length (in.)	Width (in.)	Paper thickness (in.)	Volume (cc.)	Dry weight (gm.)	Paper density (gm./cc.)	Vol. fraction in cell (c)
1	8.91	2.59	.0063	2.38	1.182	.496	.625
2	8.88	2.64	.0063	2.42	1.202	.496	.635

Volume of interlectrode space = 3.81 cc.

RESULTS

Water–Cellulose

The measured electrical values are expressed in terms of the dielectric constant and loss, ϵ'_2 and ϵ''_2, of the composite of multiple layers of paper as arranged in the dielectric cell. ϵ'_2 is equivalent to the term "dielectric value" employed by Tausz and Rumm (27) and Brown (4).

Results were obtained for water contents over the range 0 to 5.3% at frequencies between 30 and 1000 kc.p.s. These are presented as a function of temperature in Figs. 2*a* and 2*b*. Upon examination of the data certain salient trends are observed at once.

The temperature coefficient of ϵ'_2 is always positive. At the same time absorption regions occur at the temperature T_m where ϵ''_2 passes through a maximum value. At a fixed moisture content a decrease in frequency causes a shift of T_m to lower temperatures and an increase in ϵ'_2 at a particular temperature. Similar effects are shown for dry paper in Fig. 3, and are qualitative indications of dielectric relaxation due to dipole orientation according to the Debye theory (8).

Sorbed water produces interesting variations in the data. ϵ'_2 increases as has been observed previously (2, 4, 9, 27, 28). This follows logically from the high static dielectric constant of water, 80, compared with 6 for cellulose. In agreement with Veith (28) the effect is more pronounced at the higher temperatures. At the same time moisture causes a distinct increase in $(\epsilon''_2)_{max}$ (see below).

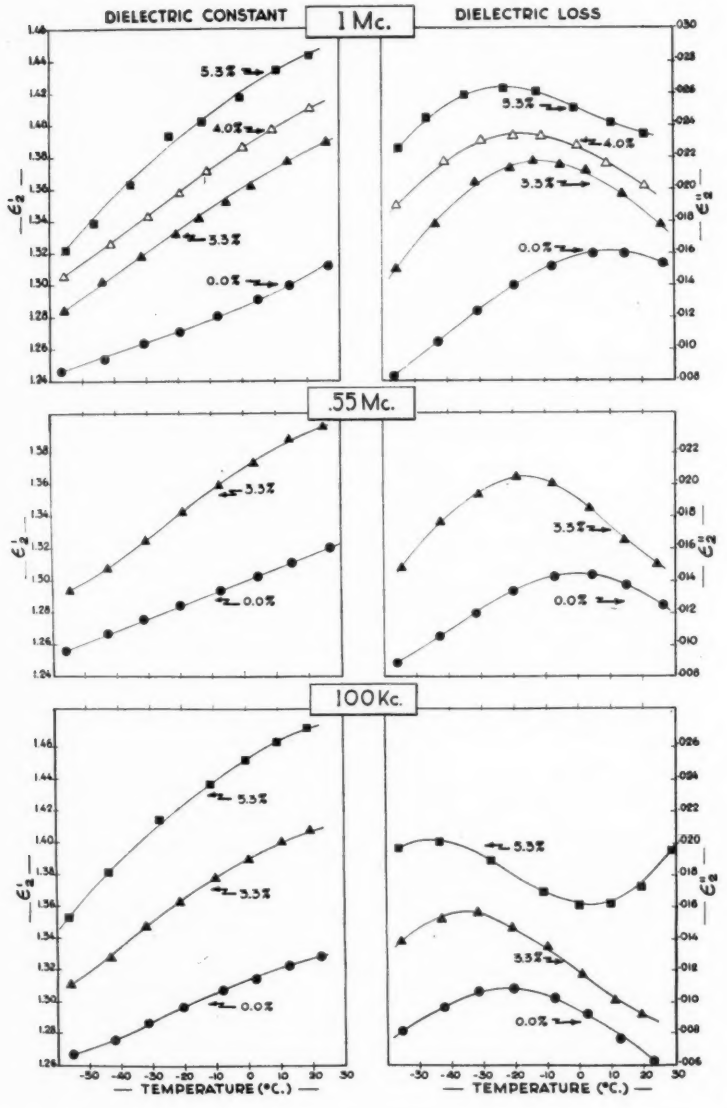


FIG. 2*a*. Dielectric dispersion at 1 Mc., 0.55 Mc., and 100 kc. of paper containing sorbed water at the inscribed percentages.

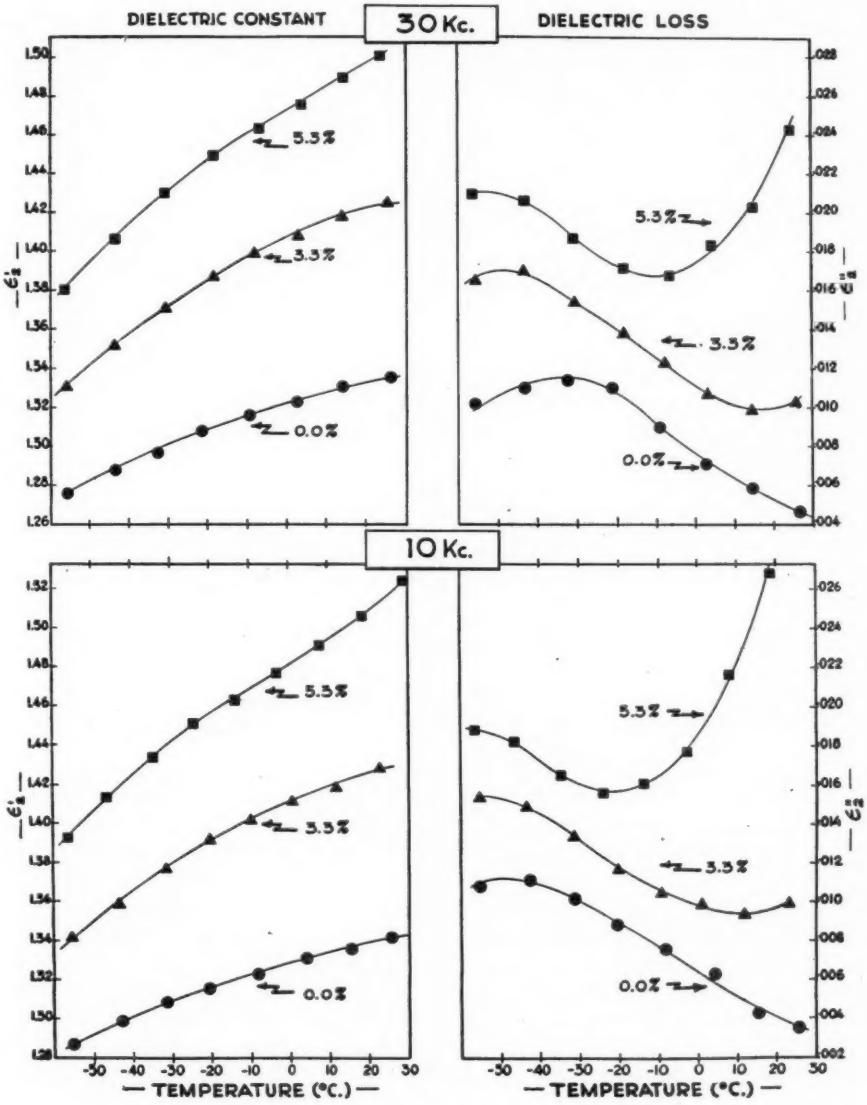


FIG. 2*b*. Dielectric dispersion at 30 and 10 kc. of paper containing sorbed water at the inscribed percentages.

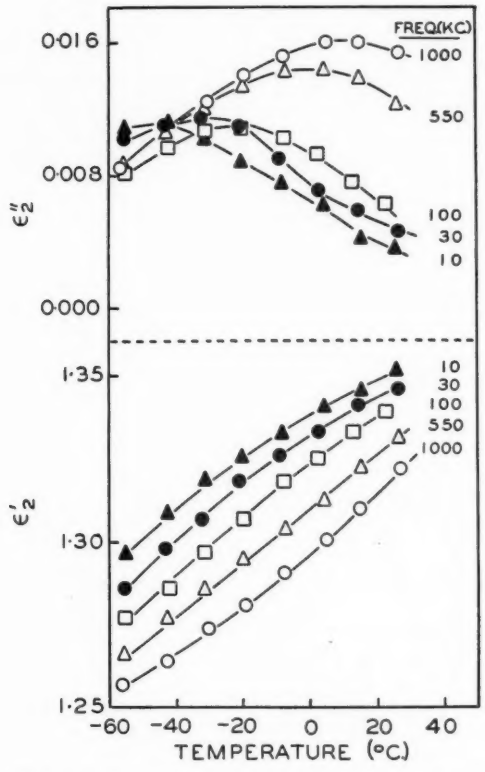


FIG. 3. Dielectric dispersion of dry paper at the inscribed frequencies.

The most significant feature of the results is the shift of T_m toward lower temperatures by an increase in moisture content. This effect, similar to that produced by a lowering in the frequency at constant moisture content, signifies a decrease in the restriction to rotation, as observed previously in several other systems (7, 14, 20, 24). T_m for dry paper at 1 Mc. was 10°C., compared with 16°C. determined from Stoops' data (26) for dry cellophane at the same frequency. The difference may be due to the residual moisture in the dry paper as defined above, Stoops having dried his sample by heating at 105°C.

A high temperature increase in ϵ''_2 is observed at the lower frequencies and the higher moisture contents. Assuming that the fractional d-c. loss is the same for paper as for the compound dielectric studied here, it is impossible to explain the high temperature rise in the loss curve in terms of ionic conductance, since there is no appreciable contribution of d-c. conductance to the measured a-c. losses. At the same time it was not experimentally feasible to establish whether a second dispersion region at a higher temperature exists such as has been observed with terylene (22).

Methanol–Cellulose

Results were obtained for methanol contents of 0.0 to 7.0% at 100, 200, 550, and 1000 kc.p.s. The results are not reported in detail since the general effect of methanol on the dispersion region was similar to that of water. There were, however, several significant differences in degree. For example, the rate of increase of $(\epsilon''_2)_{max}$ with vapor content was significantly smaller for methanol than for water, a result to be expected if the dispersion region is due to hydroxyl groups, of which there are fewer per gram of methanol than per gram of water. This point is discussed below. The more pronounced effect due to water was observed as well for the rate of increase of ϵ'_2 with vapor content at a particular temperature and frequency and for the high temperature rise in ϵ''_2. The latter is apparent in the loss curves at 100 kc. for the two cases (Figs. 2*a* and 4*a*).

In addition a characteristic break appears in the loss curves for methanol between −20 and −10°C. The effect becomes more marked at increased methanol contents as shown in Fig. 4*a*. There is no corresponding break in the dielectric constant curves (Fig. 4*b*). Furthermore, the effect appears only in the

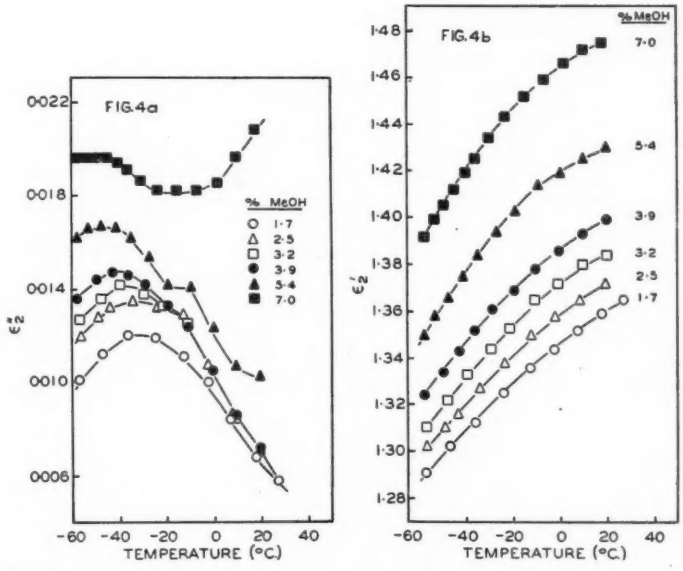


FIG. 4*a*. Dielectric loss at 100 kc. of paper containing sorbed methanol at the inscribed percentages.

FIG. 4*b*. Dielectric constant at 100 kc. of paper containing sorbed methanol at the inscribed percentages.

cases where the runs were performed by cooling. It is not observed where T_m occurs in or near the temperature range of break, as in the runs at 550 and 1000 kc.p.s.

Ethanol–Cellulose

Measurements were made at ethanol contents of 0.0 to 8.5% at 100, 200, 550, and 1000 kc.p.s. After completion of the runs on paper containing 8.5% ethanol, it was decided that each subsequent run be performed over a complete temperature cycle in order to determine the existence and the nature of the effect described above for methanol. The results at 100 kc. for paper containing 4.6% ethanol are shown in Fig. 5 and represent this effect in a typical fashion.

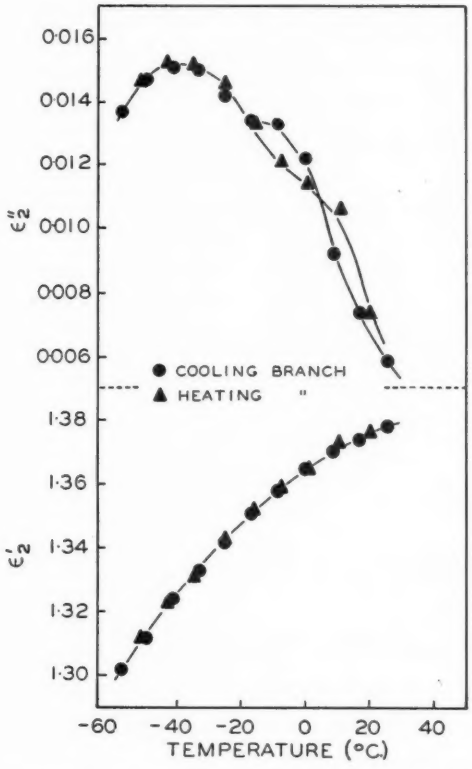


FIG. 5. Dielectric dispersion at 100 kc. of paper containing 4.6% ethanol.

It appears to be a hysteresis of some kind occurring over the temperature range −20 to 20°C. As in the case of methanol the break in the curve obtained by cooling occurs in the range −20 to −10°C., and there is no corresponding irregularity in the ϵ'_2 curves. In other respects, the results for ethanol stood in the same relation to those for methanol as the latter did to those for water. No high temperature increase in ϵ''_2 was observed in any of the ethanol curves. It was found that when $(\epsilon''_2)_{max}$ was plotted against vapor content the plots were linear within experimental error; furthermore, there was a characteristic

slope for each vapor, the same value being obtained at each of the frequencies used. The slope signifies the increase in loss due to one gram of vapor per 100 gm. dry cellulose.

In Table II the increase in loss due to 1 gm. of hydroxyl in water, methanol, and ethanol is shown. The agreement among the three values is surprisingly

TABLE II

INCREASE IN $(\epsilon''_2)_{max}$ FOR CELLULOSE DUE TO THE HYDROXYL GROUPS OF THE SORBED VAPOR

Vapor sorbed	Loss per gm. vapor	Deviation from mean, %	Molecular weight of vapor	Loss per gm. OH	Deviation from mean, %
Water	0.00188	48	18	0.0020	0
Methanol	0.00140	10	32	0.0026	30
Ethanol	0.00052	59	46	0.0014	30
	Mean = 0.00127			Mean = 0.0020	

good when one considers that the logical basis for comparison should be the area under the ϵ''_2 curves rather than $(\epsilon''_2)_{max}$. According to Reddish (22), the area under the ϵ'' vs. $\ln f$ curves is a function of the dipole moment density independent of the distribution function of **T**. In the ideal case of a single **T**, this area is $\pi\epsilon''_{max}$ so that ϵ''_{max} can be taken as a direct measure of the number of dipoles. However, when there is a distribution of **T**, this no longer applies, and one must then resort to the measurement of areas.

DISCUSSION

The arrangement in the experimental condenser was that of layers of paper alternating with layers of vapor, the layers being parallel to one another and to the electrodes. The dielectric constant and loss of this compound dielectric are referred to as ϵ'_2 and ϵ''_2, respectively. Designating the corresponding values for the paper itself as ϵ'_1, and ϵ''_1 and assuming that $(\epsilon''_1)^2 \ll (\epsilon'_1)^2$ and that the vapor layer is a pure capacitance, the following equations can be readily derived:

[1] $$\epsilon'_2 = \epsilon'_1\left[\frac{1}{c + \epsilon'_1(1-c)}\right]$$

[2] $$\epsilon''_2 = \epsilon''_1 c^{\frac{1}{2}}\left(\frac{\epsilon'_2}{\epsilon'_1}\right)^{3/2}$$

where c represents the volume fraction of paper in the cell (Table I). Equation [1] is the same as that obtained by Argue and Maass for a similar model (1). Unless otherwise stated ϵ' and ϵ'' represent the dielectric constant and loss of the cellulose fiber itself, as distinguished from ϵ'_2 and ϵ''_2, and ϵ'_1 and ϵ''_1.

In Fig. 6 are shown the loss curves at 1 Mc.p.s. for paper containing 0 and 5.3% water. Within experimental error the value of T_m appears to be the same for corresponding ϵ''_2 and ϵ''_1 curves. For 5.3% water the value of c was deter-

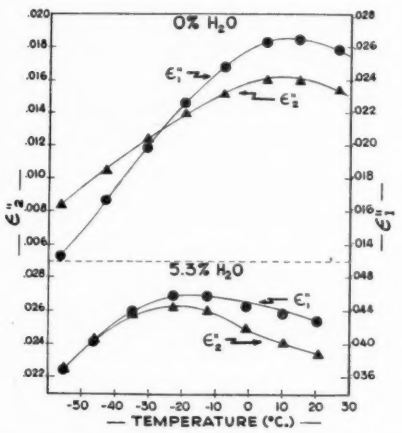


FIG. 6. Effect of the transformation of ϵ''_2 to ϵ''_1 on dielectric dispersion at 1 Mc. of paper containing 0.0 and 5.3% water.

mined as 0.635, on the assumption that the volumes of cellulose and water are additive (2), and further that the changes in volume of the fibers were duplicated in similar changes for the paper. All subsequent values of c reported were calculated on the basis of these assumptions. Because of the low coefficients of thermal expansion of cellulose (11), c varied over the temperature range covered by only about 0.2%, which is well within the experimental error.

Delevanti and Hansen (10) showed that the relationship between the density and dielectric constant of paper is expressed by a Clausius–Mosotti type of equation:

$$\frac{1}{d}\frac{\epsilon' - 1}{\epsilon' + 2} = K \qquad [3]$$

where ϵ' is the dielectric constant, d is the density, and K is a constant for a particular fiber. These results were confirmed by Calkins with an improved apparatus (5).

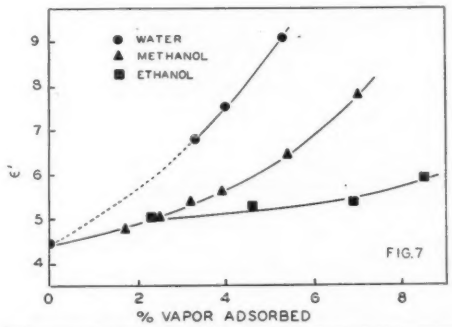
In Table III is presented, for dry cellulose at 25°C., a comparison of the results of Brown (4), Calkins (5), and the present authors, equations [1] to [3] having been employed where necessary. If it is assumed that the fibers in the samples employed were in a plane perpendicular to the electrical field, then the differences in the results of the various workers may be partly attributed to the dielectric anisotropy of cellulose. The transverse and axial dielectric constants of the cellulose crystallite have been found to be 5.27 and 7.19, respectively, at a frequency of 300 kc.p.s. (4). In cotton the fibrils are arranged spirally about the fiber axis whereas in linen they are nearly parallel to the fiber axis. Thus, when dielectric constants are measured transverse to the fiber axis, the values should increase in the order linen, linen + cotton, and cotton; the results given in Table III fall into this order.

TABLE III

DIELECTRIC CONSTANT OF DRY CELLULOSE AT 25°C.
COMPARISON OF RESULTS OF VARIOUS WORKERS

Data	Material	Freq. (kc.p.s.)	Reported values			Recalculated values		
			c	Density (gm./cc.)	Dielectric constant		ϵ'_2	ϵ'
Brown	Linen paper	300	0.648	0.610	$\epsilon'_2 = 1.363$	$c = 0.625$	1.282	3.8
Calkins	Cotton paper	1	1.000	0.8	$\epsilon'_1 = 2.42$	Density = 0.496	1.364	5.9
Present	75% linen + 25% cotton paper	300	0.625	0.496	$\epsilon'_2 = 1.334$*		1.334	5.0
		10			1.351		1.351	5.5
		1			1.357*		1.357	5.7

**Estimated from the results at other frequencies.*



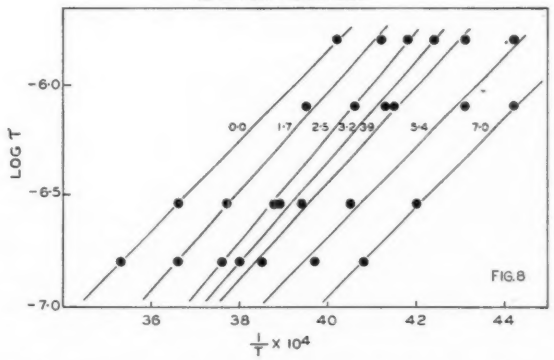


FIG. 7. Dielectric constant of cellulose at 1 Mc. and 20°C.: its variation with amount of vapor sorbed.

FIG. 8. Log T versus $1/T$ for paper containing sorbed methanol at the inscribed percentages.

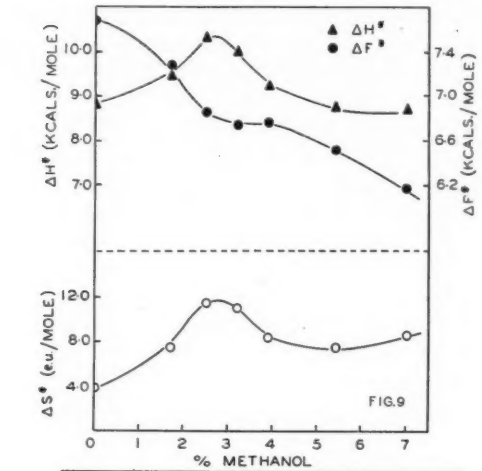
Plots of ϵ' vs. vapor content at 1 Mc.p.s. and 20°C. are shown in Fig. 7. For the calculations of ϵ' the variation of fiber density with water content was obtained from Hermans (18). This effect was slight, thus justifying the assumption that methanol and ethanol had no effect on fiber density over the range of alcohol contents covered. The rate of increase of ϵ' increases in the order ethanol, methanol, and water. At 5.3% vapor content, ethanol has produced a change in ϵ' of only 18%, while the corresponding change due to water is as high as 100%. The values of ϵ' for dry paper in the curves for water, and for methanol and ethanol, correspond to the values for paper samples No. 1 and No. 2. The difference is only 2%, which is a good check on the reproducibility of the results.

Plots of log T vs. $1/T$ were found to be straight lines, as illustrated for the methanol series in Fig. 8. From such plots it was possible to analyze the data in terms of the theory of absolute reaction rates, as briefly outlined in the introduction. From them τ was determined in each case at 298°K. These values of τ, as well as corresponding values of σ, ΔH^*, ΔF^*, and ΔS^* are presented in Table IV, σ being $\Delta \log \tau / \Delta(1/T)$.

TABLE IV
EVALUATION OF FREE ENERGY, ENTHALPY, AND ENTROPY OF ACTIVATION FOR RELAXATION FOR PAPER AT 298°K.

Vapor content	$\tau \times 10^9$ (sec.)	σ (°K.)	ΔH^* (kcal./mole)	ΔF^* (kcal./mole)	ΔS^* (e.s.u.)
% Water (gm./100 gm. dry paper)					
0.0	69.2	2060	8.84	7.68	3.9
3.3	8.2	2700	11.76	6.42	17.9
5.3	7.0	2200	9.48	6.33	10.6
% Methanol					
0.0	69.2	2060	8.84	7.68	3.9
1.7	35.5	2210	9.50	7.28	7.5
2.5	17.4	2380	10.30	6.86	11.5
3.2	14.4	2320	10.00	6.75	11.0
3.9	15.0	2160	9.27	6.77	8.4
5.4	9.9	2040	8.76	6.53	7.5
7.0	5.4	2040	8.72	6.17	8.6
% Ethanol					
0.0	69.2	2060	8.84	7.68	3.9
2.3	20.4	2350	10.16	6.95	10.8
4.6	14.6	2220	9.57	6.76	9.4
6.9	15.1	2020	8.65	6.78	6.3
8.5	5.5	2320	10.02	6.18	12.9

Considering these quantities as a function of methanol content, it appears that ΔF^* decreases continuously, passing through a plateau in the range 3 to 4%, while both ΔH^* and ΔS^* go through a pronounced maximum at 2.7% (Fig. 9). Table IV indicates that the data for water in all probability shows similar trends which are observed as well for ethanol (Fig. 10), ΔH^* and ΔS^* passing through maxima quite close to 2.7%. The minima observed, especially prominent in the case of ethanol, may possibly be a consequence of the failure of the model used at the high vapor contents at which they occur.



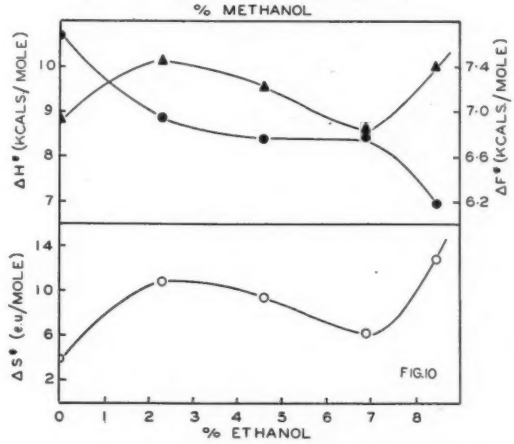


FIG. 9. Variation with % methanol of ΔH^*, ΔF^*, and ΔS^* for dielectric relaxation for paper at 298°K.

FIG. 10. Variation with % ethanol of ΔH^*, ΔF^*, and ΔS^* for dielectric relaxation for paper at 298°K.

In the neighborhood of 2.7% regain, the restriction to dipole rotation is at a maximum in all three cases. It is interesting that at this water content the density and both refractive indices of native fibers have a maximum value (18). One might expect the same to be the case for methanol and ethanol. Possibly the decrease in height of the ΔH^* and ΔS^* curves as one proceeds from water to methanol to ethanol reflects a corresponding decrease in the density effect.

In the above sense then, water as well as methanol and ethanol may be considered as having in cellulose a plasticizing action similar to that observed in other polymer systems (7, 14, 15, 24) (see Introduction).

Dielectric relaxation in starch, as in cellulose, has been attributed to the rotation of hydroxyl groups (20). It is not surprising then, in view of the similarity in structure, that the values of τ, ΔF^*, ΔH^*, and ΔS^* for starch are close to those obtained for cellulose, for example, $\Delta H^* = 7$ kcal./mole for dry starch, and 9 kcal./mole for dry cellulose. These can be compared with the value of 12.4 for a similar relaxation process in terylene (22).

The distinctness of the vapor content of 2.7% is manifested in yet another fashion. When T_m is plotted versus % methanol for each of the four experimental frequencies, one obtains the plots of Fig. 11. These plots are linear with a discontinuity at 2.5%. Above this point the slope is the same for all the frequencies, the deviation from the average being less than 1%. Below 2.5% on the other hand, the slope undergoes a marked increase with decrease in frequency.

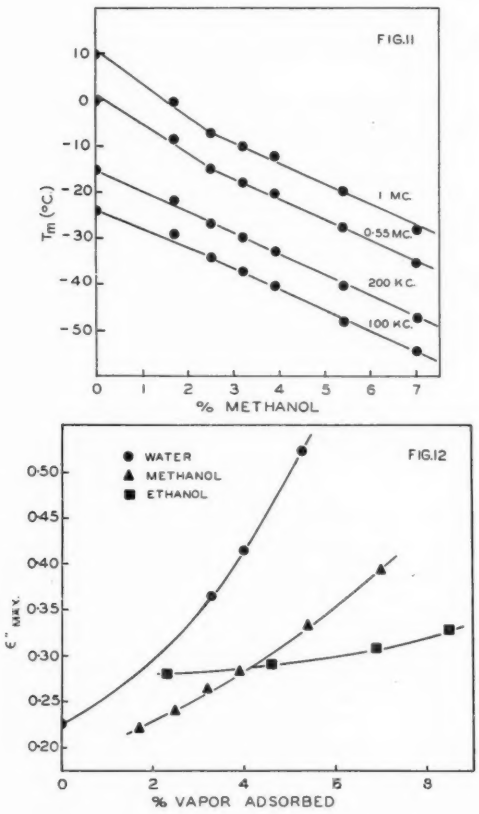


FIG. 11. Variation of T_m with % methanol at the inscribed frequencies.
FIG. 12. ϵ''_{max} for the cellulose fiber: its variation with vapor content.

According to Reddish (22), the maximum value of ϵ'' for a single relaxation time T is given by:

$$\epsilon''_{max} = \frac{2\pi}{27kT}(\epsilon_0 + 2)^2\mu^2 n$$

where k is the Boltzmann constant, T is the absolute temperature, ϵ_0 is the static dielectric constant, and n is the number of dipoles per cc. μ is the dipole moment, assumed to be 1.7×10^{-18} e.s.u. for the hydroxyl group (22). $d\epsilon''_{max}/dn$ is then given by:

$$\frac{d\epsilon''_{max}}{dn} = \frac{2\pi}{27kT}(\epsilon_0 + 2)^2\mu^2$$

assuming no change in T or ϵ_0. In this way a loss value is assigned to a single added dipole in 1 cc. of material. In order to be consistent with the convention of expressing the amount of added vapor in terms of grams per 100 gm. of dry material, a loss value is assigned to 1 gm. of added dipole in 100 gm. dry material as follows:

[4] $$\frac{d\epsilon''_{max}}{dn_c} = \frac{2\pi}{27kT}(\epsilon_0 + 2)^2\mu^2 \frac{Nd}{M(100 + P)}$$

where N is Avogadro's number, M is the weight of N dipoles, P is the percentage vapor content, and d is the density of the material.

$d\epsilon''_{max}/dn_c$ may also be obtained experimentally. The requisite ϵ''_2 data was transformed to ϵ''_1, using equations [1] and [2]. It has been shown that the dissipation factor of a paper sheet is roughly directly proportional to its density (5, 10). Using this relation, ϵ''_1 was transformed to ϵ'' for the cellulose fiber itself, using the density values employed in obtaining the plots of Fig. 7. Plots of ϵ''_{max} versus % vapor content are shown in Fig. 12. They are slightly curved, the curvature being greatest in the case of water. Doubtless this is a

TABLE V
CONTRIBUTION OF 1 GM. ADDED HYDROXYL GROUPS TO ϵ''_{max} IN CELLULOSE AND TERYLENE

Material	$d\epsilon''_{max}/dn_c$ (loss/gm. OH/100 gm. dry cellulose)		
	Calculated	Observed	Calculated/Observed
Terylene (amorphous)	0.233	0.0488	4.77
Terylene (crystalline)	0.220	0.0433	5.08
Cellulose + water	0.642	0.0834	7.70
Cellulose + methanol	0.642	0.0638	10.1
Cellulose + ethanol	0.642	0.0206	31.2

consequence of the decrease in T and the increase in ϵ_0 with increasing vapor content, the combined effect being greatest for water, presumably. From the slopes of these curves at 5.3% vapor content values of $d\,\epsilon''_{max}/dn_c$ were computed; these are presented in Table V together with those obtained from Equation [4], and the corresponding values for crystalline and amorphous terylene (22). ϵ_0 for dry cellulose was taken as 6.

It will be noticed that in this table the experimental value of $d\,\epsilon''_{max}/dn_c$ is much smaller than the theoretical value. This can be attributed to a spread of relaxation times which yields values of ϵ''_{max} considerably lower than the theoretical value (19). Even so, the reported experimental values for cellulose are probably a little high as a result of the slight magnifying effect on ϵ''_{max} of a decrease in temperature. Theoretically, one would expect $d\,\epsilon''_{max}/dn_c$ to be considerably less for terylene–water than for cellulose–water because of smaller values for ϵ_0 and d. That this is so experimentally is evidence in favor of the correctness of the model used in calculating ϵ''_{max}. The effect of changes in ϵ_0 and d is manifested as well in the smaller value of $d\,\epsilon''_{max}/dn_c$ for crystalline terylene than for the amorphous modification.

ACKNOWLEDGMENTS

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THE VISCOSITY OF SUSPENSIONS OF SPHERES: A NOTE ON THE PARTICLE INTERACTION COEFFICIENT[1]

By R. St. J. Manley[2] and S. G. Mason

ABSTRACT

Measurements of the reduced viscosity of suspensions of glass spheres 5 μ diameter have been made up to concentrations of 18% by volume. The experimental results yield the empirical equation $\eta_{sp}/c = 2.50 + 12.7c + \ldots$ The coefficient of c, due to interactions, is in fair agreement with a value of 10.05 based upon a modification of Vand's theory which takes into account the experimentally established mechanism of two-body collisions of spheres in a velocity gradient. Several reasons for the discrepancy are suggested.

INTRODUCTION

A rigorous theoretical treatment of the viscosity of a suspension of neutral rigid spheres, without Brownian motion, in a viscous fluid has been given by Vand (5) as an extension to finite concentrations of the well-known Einstein analysis at infinite dilution. Allowance is made in the theory for the increments in viscosity due to hydrodynamic interaction between the particles and to doublets formed by shear-induced two-body collisions, and the following equation, expressed as a two-term power series, is derived:

$$[1] \qquad \frac{\eta_{sp}}{c} = \frac{\eta_r - 1}{c} = \frac{\eta - \eta_0}{\eta_0 c} = \alpha_0 + \alpha_1 c + \ldots$$

Here c is the solid fraction of spheres in the suspension, η_0 is the viscosity of the medium, and η, η_r, and η_{sp} respectively are the viscosity, the relative viscosity, and the specific viscosity of the suspensions; α_0 is the Einstein coefficient ($=5/2$) and α_1 is the interaction coefficient, calculated by Vand to be 7.35.

In computing the contribution of the doublets to α_1, Vand assumed that, in a two-body collision in a velocity gradient, the participating spheres roll over one another along an arc of a great circle on each sphere and separate when the line joining their centers is perpendicular to the direction of flow. From this assumed mechanism, it was possible to calculate the collision frequency, the mean life of a doublet, and hence the steady-state concentration of doublets.

The authors (2) have made experimental observations of doublet behavior in velocity gradients and have found these assumptions invalid. It was found that the doublets rotate at constant angular velocity about an axis normal to the direction of flow and in the direction of the gradient, with no relative

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Contribution from the Pulp and Paper Research Institute of Canada, Montreal, Que.
[2]*Holder of a Fellowship from the National Research Council of Canada.*

motion between the apparent points of contact, i.e. without rolling, and that the two spheres of the doublet separate at a point which is a mirror image of the initial point of contact. While the collision frequencies were shown to be correct, the mean doublet life and, hence, the doublet concentration were found to be *exactly* twice that calculated by Vand.

If the experimentally established doublet concentration is used in the viscosity theory, the "collision time constant" r_2 (5) is doubled, and the interaction coefficient α_1 of Equation [1] becomes 10.05.

Vand made a series of viscosity measurements (6) on 130 μ diameter glass spheres suspended in zinc iodide–glycerol solutions of approximately equal density, using two Ostwald viscometers for values of c up to 50%, and a Couette viscometer for c between 35 and 55%. His experimental results yielded $\alpha_1 = 7.17$, which is in good agreement with the original theory. However, it was necessary to make large corrections for wall effects and for concentration changes due to particle crowding in the capillaries of the Ostwald viscometer. Analysis of the data shows that there is considerable scatter.

Since the corrections decrease with decreasing particle size, it was considered to be of interest to repeat the measurements using smaller spheres. This has been done with 5 μ diameter glass spheres. The precision of the measurements has been improved, and the results agree more closely with the modified theory.

EXPERIMENTAL

The spheres were made of Pyrex glass by a method due to Sollner (4). They were prepared by blowing glass, previously powdered in a ball mill, through the oxygen line feeding an ignited blow torch and collecting the particles in a tray of water. The spheres were fractionated by sedimentation in water and the fraction 1–10 μ in diameter (by microscopic measurement) was used to prepare the suspensions. When the spheres were dried by evaporating the water, aggregates formed which could not be broken up. The bonding of the spheres is believed to result from surface hydration and from the effect of the high surface tension of the water which, during the drying process, pulls the spheres into firm contact with one another. Aggregation was eliminated by replacing the water with ether by solvent exchange through acetone and ethanol, and by removing the ether under vacuum.

Homogeneous suspensions of glass spheres in zinc iodide–glycerol mixtures were prepared by dispersing measured weights of glass into measured weights of medium. Two stock solutions of zinc iodide in glycerol having densities of 2.215 and 2.342 gm./cc. at 20°C. were used. The density of the spheres (by liquid displacement) was 2.210 gm./cc.

Viscosities were measured at 20.00 ± .01 °C. in Ostwald–Fenske viscometers with capillaries 0.22 cm. in diameter. Since the solutions were hygroscopic, the viscometers were fitted with calcium chloride drying tubes.

The measured efflux times were corrected for the calculated mean density of the suspensions. The kinetic energy correction was negligible.

RESULTS

The measured relative viscosities η'_r for suspensions up to 18% by volume (the highest attempted) are listed in Table I. These have been corrected for

TABLE I
VISCOSITY MEASUREMENTS

Volume fraction c	η'_r observed	η_r corrected for wall effect	η_{sp}	η_{sp}/c
Solution No. 1 (2.342 gm./cc.)				
0	1.000	1.000	0	—
0.06375	1.206	1.209	0.209	3.278
0.0878	1.314	1.318	0.318	3.622
0.1176	1.463	1.470	0.470	3.997
0.1634	1.736	1.749	0.749	4.584
0.1838	1.863	1.879	0.879	4.782
Solution No. 2 (2.215 gm./cc.)				
0	1.000	1.000	0	—
0.04977	1.153	1.154	0.154	3.094
0.08880	1.320	1.324	0.324	3.649
0.1115	1.433	1.439	0.439	3.937
0.1401	1.583	1.592	0.592	4.226
0.1798	1.844	1.864	0.864	4.805

hydrodynamic interaction between the spheres and the wall, the effect of which has been shown in Vand's theoretical analysis (5, 6) to be equivalent to interposing a layer of pure medium between the suspension and the wall of thickness $D = 0.650\ a$, a being the diameter of the spheres. This interaction gives a pseudo-slip at the wall, and for flow through a capillary of radius R the true relative viscosity η_r is given by

$$\left(\frac{1}{\eta_r} - 1\right) = H\left(\frac{1}{\eta'_r} - 1\right) \qquad [2]$$

where the correction factor

$$H = (1 - D/R)^{-4} \qquad [3]$$

Taking the mean diameter of the spheres used in the present experiments to be 5 μ, the correction factor H was only 1.012 as compared with values of 1.178 and 1.294 in Vand's experiments (6).

Corrections for the increase in concentration due to particle crowding in the viscometer, which amounted to as much as $0.12\ c$ in Vand's experiments (6), were less than $0.005\ c$ in the present experiments and were ignored.

Fig. 1 shows a plot of values of η_{sp}/c vs. c. The points fall on a smooth straight line which, when fitted by the method of least squares, yields the equation

$$(\eta_{sp}/c) = (2.487 \pm 0.074) + (12.7 \pm 0.53)c \qquad [4]$$

where the precision is expressed as the 95% confidence limits calculated from the residual variations around the regression line.

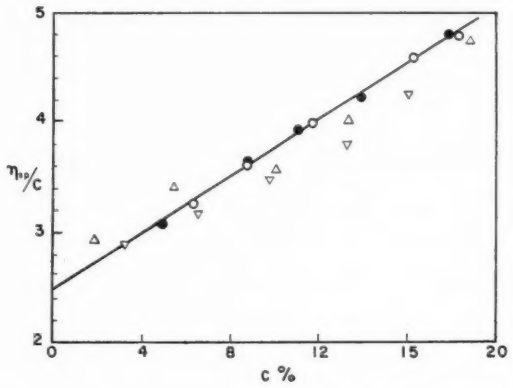

FIG. 1. Reduced viscosity – concentration plot. Vand's (5) experimental values are plotted as triangles.

The data show less scatter than those of Vand, which have been included for comparison in Fig. 1.

The first term agrees within the limit of error with the Einstein value of 5/2.

DISCUSSION

It is considered that these results provide a better experimental confirmation of Vand's theory, when modified by the experimentally established collision mechanism, than his own measurements (6). The experimental value of 12.7 for α_1 is higher than the theoretical value of 10.05.

There are several possible reasons for this discrepancy, apart from experimental error, of which the following may be cited:

(1) The collision doublets behave as rigid ellipsoids of axis ratio 2. Since the doublets are neither ellipsoidal nor rigid (2) Vand's shape factor (5) may be in error.

(2) The particles are assumed to be monodisperse, whereas spheres having a range of sizes were used. It has been shown (3) that the collision frequency is increased by polydispersity, with a possible increase in the steady state concentration of doublets and hence the collision time constant r_2. The magnitude of this effect is not known since there is no information on the mean life of polydisperse doublets. It is pointed out, however, that since the axis ratio of a doublet of spheres of unequal sizes is less than that of one of equal-sized spheres, the increase in viscosity from the increased double concentration would be offset to some extent by the decrease in the contribution per doublet.

(3) The theory assumes the particles to be neutral, i.e., the only particle interactions are due to fluid motion. However, coulombic and/or Van der Waals interactions may be appreciable for the particles used here. Calculation of the electroviscous effect for reasonable values of the ζ-potential from Booth's theoretical equations (1) show a negligible effect on α_0 for 5 μ diameter par-

ticles. It is possible, however, that the interaction term α_1 would be appreciably changed although the theory has not been sufficiently developed to estimate this effect.

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THE THERMAL DECOMPOSITION OF DIMETHYL DISULPHIDE[1]

By John A. R. Coope[2] and W. A. Bryce[3]

ABSTRACT

The thermal decomposition of dimethyl disulphide has been studied in the gaseous state by a static method. The primary reaction, which follows a reproducible induction period, produces one mole of methyl mercaptan per mole of disulphide, together with a product of low volatility believed to be a thioformaldehyde polymer:

$$CH_3SSCH_3 \longrightarrow CH_3SH + 1/n\ (CH_2S)_n.$$

There is also a competing reaction producing a large quantity of hydrogen sulphide. The remaining volatile products, hydrocarbons of two or more carbon atoms (believed to be chiefly ethylene), free sulphur, polysulphides, and carbon disulphide are formed either by the latter reaction or by the extensive decomposition of products. The decomposition is catalyzed by hydrogen sulphide, and more strongly by the complete reaction mixture. A mechanism is proposed for the main reaction.

The present investigation was undertaken as a contribution to our fragmentary understanding of the mechanisms of reactions involving the carbon–sulphur bond system in organic sulphur compounds. The C–S–S–C bond system of dimethyl disulphide was of special interest. Little is known about the thermal decomposition of the alkyl disulphides, although the thermal decomposition of aryl disulphides has received some study. The work of Schonberg, Mustafa, and Askar (10) suggests that diphenyl disulphide dissociates at the S–S bond into two free aryl thial radicals. In an early investigation Otto and Rossing (8) found that on distillation at atmospheric pressure diamyl disulphide (b.p. 248° C.) gradually decomposes into sulphur or sulphur-rich substances and a tarry residue. Bezzi (3) reported that dioctyl disulphide decomposes at its boiling point of 190° C. at 15 mm. Faragher, Morrell, and Comay (7) found that decomposition of vaporized naphtha solutions of various alkyl disulphides at 496° C. produces the corresponding alkyl mercaptan, hydrogen sulphide, free sulphur, alkyl sulphides, thiophenes, and saturated and unsaturated hydrocarbons.

In some preliminary experiments in this laboratory it was found by Patrick (9) that dimethyl and diethyl disulphides decompose above 300° C. yielding complex pressure–time curves. The homogeneous decomposition of dimethyl disulphide was found to produce large amounts of mercaptan and hydrogen sulphide.

EXPERIMENTAL

Reagents

The dimethyl disulphide, obtained from Eastman Kodak Co., Rochester, New York, gave negative tests for mercaptans, hydrogen sulphide, free

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Contribution from the Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada. From a thesis presented by J.A.R.C. to the University of British Columbia in partial fulfilment of the requirements for the degree of Master of Science.
[2]*Present address: Wadham College, Oxford, England.*
[3]*Assistant Professor.*

sulphur, and carbon disulphide. Its refractive index of $n_D^{20} = 1.5261 \pm 0.0002$ agreed well with Vogel and Cowan's (12) value of 1.5260. It was fractionated in a vacuum apparatus before use. The pure hydrogen sulphide was prepared by the method of Bickford and Wilkinson (4). The other sulphur compounds were fractionated Eastman Kodak products.

Apparatus

The apparatus was an all-glass static system consisting essentially of a heated 250 ml. pyrex reaction vessel connected to an evacuating system, a sampling system, and to storage vessels for the reactants. To avoid difficulties of corrosion and condensation, a glass spoon-type Bourdon gauge was used for pressure measurement. The gauge was used both as a direct measuring instrument and as a null indicator.

The volatile constituents of the reaction mixture were sampled in gas pipettes which were attached to the capillary connections of the reaction vessel. From the results of the analyses of the contents of these pipettes the partial pressures of various substances in the reaction vessel during decomposition were calculated. The less volatile constituents were collected in a dry ice trap and analyzed qualitatively.

Analytical Methods

Carbon disulphide was estimated colorimetrically by means of its reaction with cupric acetate and piperidine (5). Thiophenes were tested for with isatin solution (1). Free sulphur was determined in an AnalaR petroleum ether solution of the sample by the method of Ball (2) using dilute reagents.

Hydrocarbons were estimated approximately by a crude gas fractionation method: hydrogen and methane could be separated off at liquid nitrogen temperature. The remaining hydrocarbons were separated off at the freezing point of *n*-pentane, −130° C., and their pressure was corrected slightly for hydrogen sulphide.

The methods of analysis for mixtures of hydrogen sulphide, methyl mercaptan, and disulphide were developed in this laboratory, and are being reported elsewhere in more detail (6). Hydrogen sulphide was absorbed in dilute base, precipitated as cadmium sulphide, and separated from mercaptan by filtration through asbestos in 0.005 *M* acid. The cadmium sulphide precipitate was oxidized directly with excess acidified standard iodine and determined by back titration with thiosulphate. This method was sensitive to less than 2.5×10^{-6} moles of hydrogen sulphide (0.5 mm. pressure in the reaction vessel) and was accurate in the presence of mercaptan to within 3%. The direct determination for hydrogen sulphide made it possible to determine mercaptan indirectly from the total sulphydryl content of the reaction mixture as determined by absorption in excess standard iodine and back titration with thiosulphate.

In Ball's method (2) for the determination of disulphides the disulphides are reduced to mercaptans by refluxing with zinc and glacial acetic acid. In the present work AnalaR petroleum ether was used as the solvent. By using a slightly stronger acid (94%), a lower temperature (water bath), and by

heating long enough to transfer the entire methyl mercaptan formed to a trap, it was possible to obtain results with a reproducible error in the range $110\frac{1}{2} \pm 1\frac{1}{2}\%$ reduction. The analyses were corrected appropriately. Unfortunately some of the actual analyses were invalidated by the interference of alkyl polysulphides, compounds of the type R–S_x–R, which reduce to mercaptan and hydrogen sulphide.

The presence of alkyl polysulphides was inferred from an interference with the disulphide determinations and by a reaction with mercury. It was observed that a solution of the volatile products in petroleum ether, although free of elementary sulphur, reacted with metallic mercury to produce a black crystalline compound. This was attributed to a reaction of the type quoted by Sidgwick (11):

$$2\ Hg + CH_3S_4CH_3 \rightarrow 2\ HgS + CH_3SSCH_3.$$

RESULTS

A typical family of pressure–time curves for the decomposition of dimethyl disulphide is presented in Fig. 1. There is an initial rapid pressure decrease, followed by a period of constant pressure, after which the rate rises slowly to

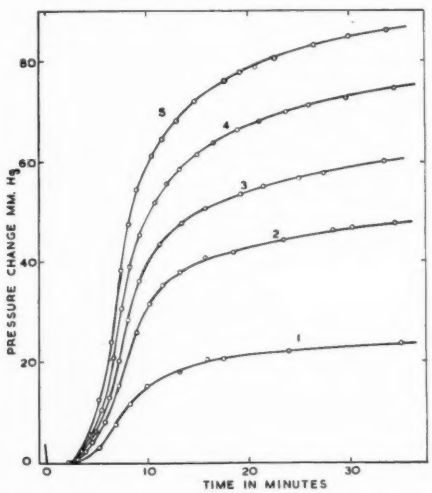


FIG. 1. Pressure–time curves for the decomposition of dimethyl disulphide at 341° C. Initial pressure of disulphide respectively (1) 24.0, (2) 57.5, (3) 73.0, (4) 92.5, (5) 108.0 mm.

a maximum. The induction period was reproducible: in a series of 16 runs at 316° C. it had a mean length of 11.6 min. with standard deviation only 0.7 min.

The results of extended experiments showed that, after the rate had decreased quite sharply from the maximum to a low value, there remained a slow residual reaction which continued for some time. This behavior suggests the decomposition of products. Both at 341° C. and at 373° C. the final pressure increase is greater than 105% of the minimum pressure.

Effect of Packing the Reaction Vessel

A sixfold increase in the surface to volume ratio was achieved by packing the vessel with short lengths of pyrex glass tubing. The induction period and maximum rate of reaction were unaffected, indicating that the decomposition is a homogeneous process. The only effect was a slight reduction of the final pressure, attributable to increased adsorption of the products on the vessel surface.

The Initial Pressure Decrease

By using the Bourdon gauge as a direct reading instrument and by using relatively low pressures, it was possible to fill the reaction vessel in times as short as two seconds. It was possible, therefore, to observe the greater part of the initial pressure decrease. With 95 mm. of disulphide at 316° C. the pressure decrease was about 15 mm., the initial rate of the decrease was of the order of 2 mm. per second, and the process was approximately 90% complete in 15 sec. The magnitude of the decrease was greater at higher initial pressures and at lower temperatures; it was only slightly increased by packing the reaction vessel.

Analysis showed that during the induction period the reaction mixture consists almost entirely of unreacted disulphide. This fact suggested strongly that the pressure decrease is due to adsorption of the reactant disulphide on the walls of the pyrex reaction vessel. Further observations supported this view: (1) A few millimeters pressure of hydrogen sulphide in the reaction vessel reduced the extent of the decrease by 80%. Hydrogen sulphide is known to adsorb on glass. (2) If a part of the reactant were removed from the vessel during the induction period, a short, rapid pressure increase occurred, indicating desorption of the disulphide.

An estimation of the activation energy of the initial rate of the pressure decrease gave a value of 16 kcal. per mole. Whereas this is much less than the usual energies of pyrolytic reactions, it is of the order of magnitude of energies of adsorption. It leads to a frequency factor of 10^4 sec^{-1}. If a simple collision theory of adsorption is accepted, this frequency factor should be equal to the number of times a molecule strikes the wall per second. The latter was calculated from kinetic theory as 1×10^4 $sec.^{-1}$ at 316° C.[4] This excellent agreement is considered additional proof that the initial pressure decrease is due to adsorption.

Dependence of the Rate on Initial Disulphide Pressure

The minimum pressure of the induction period was found to be a suitable 'initial' pressure for correlating the results of different experiments. There is little doubt that it represents the true initial disulphide pressure at the start of the main reaction.

The initial pressure was varied from 24 mm. to 230 mm. at 341° C. The dependence of extent of reaction on the initial pressure is given in Table I. Per cent pressure increases are listed for several reaction times. The results

[4] *From kinetic theory the "collision number" is* $\frac{1}{4}S(8RT/M)^{\frac{1}{2}}$, *where S is the surface to volume ratio of the reaction vessel and M is the molecular weight. S = 1, M = 94, T = 589° K.*

TABLE I
DEPENDENCE OF THE EXTENT OF REACTION ON THE INITIAL PRESSURE. $T = 341°$ C.

Initial pressure, mm.	% pressure increase after: 8 min.	10 min.	15 min.	20 min.
24.0	45	62	76	85
57.5	36	53	68	74
73.0	38	54	68	74
92.5	38	53	66	73
108.0	43	54	68	73
141.8	35	48	63	68
166.5	42	53	68	74
229.5	42	54	68	73

show a first order dependence. The rate constants calculated from these data had a mean value of 20.8×10^{-4} sec.$^{-1}$ at 341° C. with a standard deviation of 0.7×10^{-4} sec^{-1}.

At pressures below 150 mm. (temperature 341° C.) the induction period is independent of the initial pressure, but at higher pressures its length is reduced. The time at which the maximum rate occurs varies in the same way.

Dependence of the Rate on Temperature

The significant results are shown in Table II. A plot of ln k vs. $1/T$ gave a straight line from which an over-all activation energy of 45 ± 4 kcal. per mole was calculated. The frequency factor was estimated to be 2×10^{13} sec^{-1}.

TABLE II
DEPENDENCE OF THE REACTION ON TEMPERATURE

Temperature, °C.	Induction period, sec.	Time of max. rate, sec.	Rate constant, sec.$^{-1}$
316	690	1860	0.00042
314	120	420	0.00208
360	35	157	0.0067
373	19	65	0.0116

Analytical Results

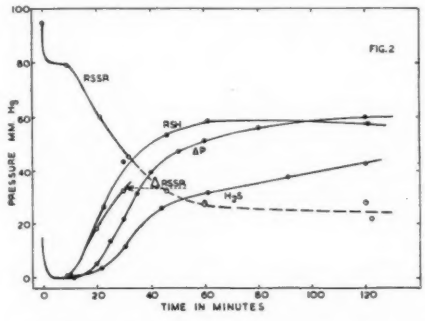
A temperature of 316° C. and an initial pressure of 80 mm. were the standard conditions used for experiments in which analyses were done for the components of the reaction mixture.

Qualitative analyses of the reaction mixture showed that thiophenes are formed in traces only. The principal volatile products were hydrogen sulphide, mercaptan, carbon disulphide, alkyl polysulphides, and low boiling hydrocarbons of two or more carbon atoms. Hydrogen and methane were not detected; if present at all they appear to total less than 5% of the hydrocarbon. The mercaptan was identified as chiefly or entirely methyl mercaptan by the yellowish-green color of its silver mercaptide; the higher silver mercaptides are white. Of the products which were not sampled by the gas pipettes, free sulphur was identified amongst the accumulated products in the cold trap. An

involatile tar was formed in considerable quantity; it appeared black by reflected light and reddish-brown by transmitted light.

The two volatile products formed in largest quantity were methyl mercaptan and hydrogen sulphide. The results of quantitative analyses were used to construct partial pressure-versus-time curves for these two products and for the reactant disulphide. These curves, with other results, are shown in Fig. 2. During the early stages of the reaction the rate of hydrogen sulphide formation is equal to one half the rate of increase in pressure. The rates become nearly equal in the later stages.

The alkyl polysulphides in the reaction mixture interfered so seriously with the determination of disulphide that the only accurate determinations were those which were made in the initial stages of the decomposition. A curve labelled *RSSR*, showing the disappearance of disulphide is given in Fig. 2. The values for the dotted part of the curve are believed to be much too high owing to interference by polysulphides. The estimated pressure of disulphide during this part of the reaction is approximately zero since the main reactions appear to be over at 60 min. A curve representing the amount of disulphide decomposed in the early stages of the reaction is also plotted. It was constructed by subtracting the disulphide present from the initial pressure.



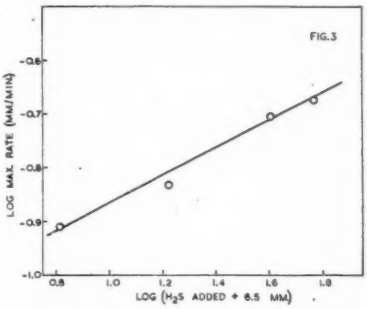


FIG. 2. Analytical results for the "standard" reaction, $T = 316°$ C., $P_{min} = 80.0$ mm. *RSSR* shows analytical results for disappearance of disulphide. $\Delta RSSR$ shows measured amount of disulphide decomposed.

FIG. 3. Dependence of the maximum rate on added hydrogen sulphide. Constant disulphide pressure, 52.2 mm. Temperature, 316° C.

Fig. 2 shows that the reaction producing mercaptan is distinct from that producing hydrogen sulphide. The former appears to reach its maximum rate before 20 min., whereas the latter reaches its maximum rate only after 30 min. The end of the induction period appears to be the same for both reactions. Since the pressure increase does not appear to occur until H_2S is formed, the formation of mercaptan must involve little or no pressure change. This is well illustrated by the fact that at 15 min. with a mercaptan pressure of 10 mm. the total pressure change by all processes is only $1\frac{1}{2}$ mm. Moreover, the reaction producing hydrogen sulphide must account also for much of the remaining volatile products. The reactions which occur after 60 min., the slow

formation of H_2S for example, appear to be reactions amongst the decomposition products. Probably a number of complex processes occur simultaneously.

The partial pressures of all the volatile constituents of the reaction mixture were measured at 120 min., after the completion of the main reactions. The results of analyses are listed in the first column of Table III. The values for carbon disulphide and for hydrocarbons are significant to the order of magnitude only. Estimates of the remaining constituents are recorded in the second column of Table III. The order of magnitude figure for polysulphides was

TABLE III
VOLATILE CONSTITUENTS OF THE REACTION MIXTURE AFTER 120 MIN. OF REACTION AT 316° C. (P_{min} = 80 MM.)

Analytical pressures, mm.		Estimated pressures,[a] mm.	
CH_3SH	59	CH_3SSCH_3	0
H_2S	42	$CH_3S_xCH_3$	8
CS_2	15	S_8	0
Hydrocarbons (C_2)	25		
$H_2 + CH_4$	0		
Thiophene	1		

Measured total pressure 140 mm.

[a] *See text.*

estimated by assuming an apparent 25 mm. of disulphide, shown by the disulphide test, to be due in reality to tetrasulphide. Elemental sulphur could not be determined quantitatively, but it appeared to be present in small amounts only. Since it exists at 317° C. almost entirely as S_8, its necessarily small pressure has been listed as zero.

Effect of Added Hydrogen Sulphide

The addition of hydrogen sulphide to the reaction mixture had a marked effect on the rate of reaction. The induction period and the period of autoacceleration were shortened, and the maximum rate was increased. The significant results are listed in Table IV. In each case the maximum rate of

TABLE IV
EFFECT OF HYDROGEN SULPHIDE ON THE DECOMPOSITION OF 52.3 MM. OF DISULPHIDE AT 316° C.

Added H_2S, mm.	Induction period, min.	Time of max. rate, min.	Maximum rate, mm./min.
0.0	13	34.0	0.123
10.2	$4\frac{1}{2}$	20.5	0.147
34.0	$2\frac{1}{2}$	12.0	0.198
52.0	$1\frac{1}{4}$	9.7	0.213

pressure rise (also of hydrogen sulphide formation) occurred after a total pressure increase of 13.7 mm., corresponding in a normal decomposition to the formation of 6.5 mm. of hydrogen sulphide. The logarithm of 'the added

hydrogen sulphide plus 6.5 mm.' is plotted in Fig. 3 against the logarithm of the maximum rate. The graph is roughly linear, suggesting that the amount of hydrogen sulphide present at the maximum rate is, in fact, the normal amount, plus the amount added. The slope of 0.25 indicates approximately a rate dependence to the one quarter power, at least at the time of the maximum rate: i.e., with disulphide constant,

$$d\ H_2S/dt = k\ [H_2S]^{\frac{1}{4}}.$$

The total pressure increase was independent of the amount of added hydrogen sulphide. This suggests that the final ratio of hydrogen sulphide formed to mercaptan is unchanged by the addition of hydrogen sulphide. The general character of the decomposition appears entirely unaffected. If this is so the hydrogen sulphide must also accelerate the reaction producing mercaptan.

Effect of Added Mercaptan

A decomposition in the presence of methyl mercaptan at a pressure equal to 30% of the disulphide, did not differ significantly from the normal. Hence, mercaptan is simply an end product of the decomposition.

Effect of the Complete Reaction Mixture

The effect of the complete decomposition products on the reaction was investigated by admitting a second sample of disulphide to the reaction vessel after the completion of a previous experiment. The induction period was reduced to a much greater extent than can be attributed to hydrogen sulphide alone. Indeed, the true induction period of the mercaptan reaction may have been removed entirely. In contrast to the effect of hydrogen sulphide alone the complete reaction mixture did not accelerate the maximum rate of pressure rise. The final pressure increase was slightly less than for the normal reaction.

Effect of Nitric Oxide

In the presence of 0.6, 2, and 7% nitric oxide, the induction period was no longer reproducible but the maximum rate was normal and occurred at the usual time.

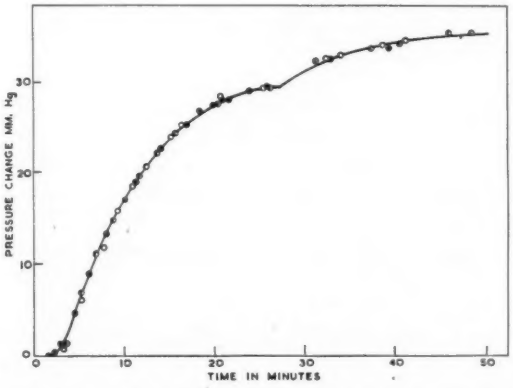


FIG. 4. Decomposition of diethyl disulphide at 318° C. Initial pressure, 28.0 mm. Results of three experiments are superimposed.

Comparison with the Decomposition of Diethyl Disulphide

The decomposition of diethyl disulphide appeared to be considerably different from the decomposition of dimethyl disulphide. Three superimposed pressure–time curves are presented in Fig. 4. Although similar in form to those of dimethyl disulphide they show a much greater total pressure increase. The maximum rate is first order with respect to the initial pressure, except at low pressures. The main rate constant of $19.7(\pm 1.1) \times 10^{-4}$ sec.$^{-1}$ at 318° C., obtained from runs at 28 mm., 33 mm., and 40 mm., falls off between 28 and 18 mm. This rate is of the same order as that for dimethyl disulphide at the much higher temperature of 341° C. The decomposition of diethyl disulphide produces an involatile tar similar in appearance to that produced by dimethyl disulphide. Unlike the decomposition of dimethyl disulphide, it produces a considerable quantity of a fine yellow solid, presumed to be elemental sulphur.

One feature of Fig. 4 is the "break" in the curve near the 30-min. mark. This suggests that the reaction may involve a second stage which is largely responsible for the pressure increase after 30 min.

DISCUSSION

The over-all reaction for the decomposition of dimethyl disulphide is complex. Two main reactions appear to occur. The first is decomposition of the disulphide with the formation of mercaptan, and the second is the formation of hydrogen sulphide and allied products. Both reactions exhibit an induction period. Extensive decomposition of the products of these reactions also takes place.

The rate curves for the formation of mercaptan and H_2S show that the decomposition of the disulphide comes to an end after about 60 min. for the 'standard reaction', i.e., the reaction illustrated in Fig. 2. This behavior cannot be due to an equilibrium as neither the addition of mercaptan nor the addition of hydrogen sulphide to the reaction mixture has any effect on the final pressure. Nor can it be due to inhibition by the products. It must be concluded that the pressure of the reactant disulphide falls to zero after about 60 min. Accordingly, the disulphide pressure at 120 min. has been listed in Table III as zero.

Hydrogen sulphide and mercaptan, the two products formed in greatest quantity, are both reduced relative to the disulphide. To balance the hydrogen, the hydrocarbon products must be either unsaturated or polymeric (Table III). Since the formation of hydrocarbons of more than two carbon atoms appears unlikely, and, indeed, could not account for the magnitude of the pressure increase, it is suggested that the hydrocarbons may be chiefly or entirely ethylene.

From Table III the estimated pressures of the components of the reaction mixture at 120 min. total 148 mm. This value agrees satisfactorily with the measured total pressure of 140 mm., and suggests that no other volatile products are formed in quantity. It supports the conclusion that the disulphide pressure is zero.

The primary reaction is believed to be the decomposition of one mole of disulphide to form one mole of methyl mercaptan. Since there is no accompanying pressure change the remaining fragment "CH_2S" of the dimethyl disulphide molecule must be removed from the system in some way. The thioaldehydes are well known for their remarkable tendency to polymerize; they are scarcely known in the monomeric state (11). The normal polymerization to cyclic trithioformaldehyde would result in a small pressure increase, but in the presence of foreign free radicals the polymerization would presumably be to higher polymers which are involatile. The following process, for example, would not allow ring closure:

$$R \xrightarrow{CH_2=S} RSCH_2 \xrightarrow{CH_2=S} RSCH_2SCH_2$$

The presence of an involatile tar in the reaction products lends support to this view. If this polymerization mechanism occurs, the primary decomposition may be represented by the following over-all reactions:

$$\begin{aligned} CH_3SSCH_3 &\longrightarrow CH_3SH + CH_2=S \\ n\ CH_2=S &\longrightarrow (CH_2S)_n \end{aligned} \qquad [I]$$

Hydrogen sulphide appears to be produced by two reactions. The main reaction occurred under the conditions of these experiments between 10 and 60 min.; the total hydrogen sulphide produced by it is approximately 27 mm.; clearly its rate depends on the disulphide present. The second reaction became evident after the disulphide had disappeared. In the experiments discussed here it produces 10 mm. of hydrogen sulphide between 60 and 120 min. at a nearly constant rate, and would appear, therefore, to account for at least 5 mm. (15%) of the hydrogen sulphide produced before 60 min. This reaction must be due to the decomposition of products of the two main reactions, perhaps polythioaldehyde or alkyl polysulphides.

The disulphide available for the main reaction producing hydrogen sulphide appears to be equal to the hydrogen sulphide produced by it. This disulphide can be estimated by subtracting from the initial disulphide pressure the amount used up in producing mercaptan and polysulphide, 59 mm. and approximately 8 mm., respectively. The reaction producing mercaptan seems well established and the mercaptan analysis appears reliable. The polysulphide is in any case only a small correction and therefore the result of 28 mm. of disulphide available for hydrogen sulphide formation should not be greatly in error. It is roughly equal to the hydrogen sulphide produced. Thus one mole of disulphide appears to produce one mole of hydrogen sulphide in the main reaction. This suggestion appears consistent with the observed pressure change, whatever the complete reaction may be. There are, however, many factors affecting the pressure change and a certain deduction is difficult.

The alkyl polysulphides may be formed by addition reactions of the following type:

$$CH_3SSCH_3 + S_x \longrightarrow CH_3S_{x+2}CH_3 \qquad [II]$$

The labile character of polysulphide chains is well known.

The 25 mm. of hydrocarbons found by analysis from the standard experiment appear to be almost entirely ethylene. The ethylene could be formed by

a second decomposition reaction along with the H_2S, as follows:

$$CH_3SSCH_3 \longrightarrow H_2S + CH_2{=}CH_2 + S \qquad [III]$$

This equation, though speculative, is consistent with the data available. The estimate for ethylene is in the ratio one-to-one with those for hydrogen sulphide and disulphide. When taken together, the three reactions postulated would account reasonably for all the substances observed in the decomposition. The reactant disulphide and the products hydrogen sulphide, mercaptan, and hydrogen, would be accounted for completely. The elemental sulphur of reaction [III] would produce the polysulphides of reaction [II] together with traces of S_8. Carbon disulphide, the only other volatile product could well be attributed to the secondary reactions, to the decomposition of the tar, for example. It is difficult to see how it could be produced from the disulphide directly. Finally, the amount of monomeric thioaldehyde necessary to balance reaction [I] would account quite well for the quantity and composition of the involatile products at 120 min., together with the carbon disulphide and small amounts of secondary hydrogen sulphide.

Although no direct evidence was obtained of the occurrence of free radical chains in the decomposition of dimethyl disulphide, it seems unlikely that the entire decomposition could take place by simple molecular reactions. The complexity of the reactant, the variety of the products, and the peculiar rate laws, all suggest free radical mechanisms.

For the primary reaction a straightforward unimolecular decomposition into methyl mercaptan and thioformaldehyde can be conceived. However, this reaction, being unimolecular, could not be catalyzed by the products, and therefore an explanation of the induction period on this basis would be difficult. On the other hand, a free radical chain mechanism is plausible.

The initiating radical might be CH_3S arising from the dissociation of disulphide at the S–S bond:

$$CH_3SSCH_3 \longrightarrow 2\ CH_3S \qquad [1]$$

The following sequence could result:

$$CH_3S + CH_3SSCH_3 \longrightarrow CH_3SH + CH_3SSCH_2 \qquad [2]$$

$$CH_3SSCH_2 \longrightarrow CH_2{=}S + CH_3S \qquad [3]$$

In addition to producing mercaptan to the required extent this mechanism also produces the postulated thioformaldehyde. Polymerization of the latter could arise through:

$$n\ CH_2{=}S \longrightarrow (CH_2S)_n \qquad [4]$$

$$\text{or } CH_3SSCH_2 + CH_2{=}S \longrightarrow CH_3SSCH_2SCH_2 \qquad [5]$$

A second possibility for the initiating radical of equation [1] is the production of a sulphur atom through an intermediate rearrangement of the type:

$$CH_3SSCH_3 \longrightarrow CH_3{-}\underset{\ddot{S}}{S}{-}CH_3 \longrightarrow S + CH_3SCH_3 \qquad [6]$$

through the decomposition of polysulphides:

$$CH_3S_xCH_3 \longrightarrow S + CH_3SS_{x-1}CH_3 \qquad [7]$$

or through the reaction [III] postulated for the production of hydrogen

sulphide. The observed catalysis by hydrogen sulphide may be due to the production of sulphur atoms by a reduction process:

$$H_2S + CH_3SSCH_3 \longrightarrow S + 2CH_3SH \qquad [8]$$

The more marked catalyses by the complete reaction mixture could be attributed to reaction [7]. The autoacceleration and approximate coincidence of the induction periods of the mercaptan and hydrogen sulphide reaction could also be dependent on the production of sulphur atoms.

More experimental work must be done before the details of the over-all reaction can be understood.

ACKNOWLEDGMENTS

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THE CHARACTERIZATION OF DELCOSINE AND SOME OF ITS DERIVATIVES[1]

By W. I. Taylor,[2] W. E. Walles,[3] and Léo Marion

ABSTRACT

Reanalysis of delcosine and several of its derivatives shows that the most likely empirical formula is $C_{24}H_{39}O_7N$. Delcosine has been shown to be identical with Goodson's base C. Acetylation produces monoacetyldelcosine, identical with Goodson's naturally occurring base B. It has been possible to prepare two isomeric diacetyl derivatives, one of which has been reported previously, and a further acetylated compound also reported previously which seems to have lost the elements of water. A dipropionyldelcosine is also described. The base contains three methoxyls and four hydroxyls, only two of which are acetylated readily.

Delcosine, one of the alkaloids of *Delphinium consolida* L., has been assigned several empirical formulae by various authors, i.e., $C_{21}H_{33}O_6N$ (5), $C_{25}H_{40}O_7N$ (*sic*) (1), and $C_{22}H_{37}O_6N$ (4). In order to arrive at a more definite formula, the alkaloid was purified and reanalyzed together with some salts and a number of its derivatives. The empirical formula which appears to agree best with all the results is $C_{24}H_{39}O_7N$. On this basis the base, which is tertiary, contains three methoxyls and four active hydrogens (Zerewitinow) corresponding to four hydroxyl groups, thus accounting for all the oxygen. Delcosine further contains an N-alkyl which is probably an ethyl (3). The pK_A of the alkaloid is 6.49. The formula can be expanded to $C_{19}H_{21}(NC_2H_5)(OCH_3)_2(OH)_4$ containing a C_{19} nucleus in agreement with that of a number of aconite and delphinium bases (2).

From *Delphinium ajacis* Goodson (3) had isolated in small quantity a base which he designated "alkaloid C" for which he proposed the empirical formula $C_{24}H_{37}O_7N$. This base contained an N-ethyl group and resembled delcosine in its properties. A sample of "alkaloid C" kindly supplied by Dr. T. M. Sharp has now been shown by direct comparison to be identical with delcosine. The melting points of the bases and that of the mixture were identical and the infrared absorption spectra were superimposable.

Two of the four hydroxyls of delcosine underwent acetylation more readily than the other two. It has been possible to prepare a monoacetyldelcosine, a diacetyldelcosine, a monotrichloroacetyldelcosine, and a dipropionyldelcosine. Diacetyldelcosine is quite distinct from the "triacetyldelcosine" already reported (4) which, on the basis of the new formula, is also a diacetyldelcosine. The infrared spectra of these two isomers show marked differences.

Among the alkaloids of *D. ajacis* Goodson (3) had reported the presence of a minor base, "alkaloid B", which gave rise to "alkaloid C" on hydrolysis and

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[3]*National Research Council of Canada Postdoctorate Fellow.*

was considered as an acetyl derivative. A sample of "alkaloid B" kindly supplied to us by Dr. T. M. Sharp indeed proved by melting point, mixed melting point, and comparison of the infrared absorption spectra to be identical with monoacetyldelcosine.

The alkaloid delphamine isolated by Rabinovich and Konowalowa (6) from an unidentified *Delphinium* species may possibly be identical with delcosine. It is not possible to conclude this definitely without a direct comparison, but the recorded melting points of the two bases, of their hydriodides, bitartrates, chloroplatinates, and the diacetyl derivatives are remarkably similar.

The acetyl derivative of melting point 159–161° reported by Marion and Edwards (4) has again been prepared. The infrared absorption spectrum of this derivative contained no absorption bands in the hydroxyl region, and the absence of hydroxyl groups thus indicated was confirmed by an active hydrogen determination which gave negative results. The analytical figures did not agree with the requirements of a tetraacetyl derivative, but were in best agreement with a diacetyldelcosine having lost the elements of water. Since no hydroxyl was present the fourth hydroxyl oxygen must have become involved in a cyclic ether or converted to a carbonyl.

A derivative was also obtained in one experiment which appeared to be tetraacetyldelcosine, but will require further characterization before its identity is established.

EXPERIMENTAL[4]

Delcosine was purified by repeated crystallization from dioxane – petroleum ether (1:1), m.p. 203–204°. Found: C, 63.76, 64.04, 63.83; H, 9.07, 8.93, 9.01; N, 3.09, 3.18; OCH_3, 20.14, 20.75; N-alk., 7.85, 7.83; act. H (Zerewitinow), 0.75, 0.85%; mol. wt. (by titration), 455. Calc. for $C_{24}H_{39}O_7N$: C, 63.55; H, 8.67; N, 3.09; 3 OCH_3, 20.53; 4 act. H, 0.88; $N.C_2H_5$, 6.39%; mol. wt. 453.6. pK, 6.49 (value of pH at half titration in 50% methanol with 0.0333 *N* hydrochloric acid). In admixture with Goodson's "alkaloid C" (3) the melting point was unchanged. The infrared absorption spectra of delcosine and "alkaloid C" were superimposable. The spectrum of delcosine contained the following peaks:[5] 3518 (43), 3476 (57), 3362 (73), 1355 (58), 1325 (48), 1305 (67), 1275 (48), 1225 (64), 1192 (69), 1170 (64), 1140 (70), 1115 (89), 1095 (85), 1085 (88), 1050 (68), 1040 (72), 1015 (62), 1000 (47), 980 (45), 970 (56), 950 (81), 915 (27), 875 (37), 860 (41), 815 (25), 800S (22), 760 (45), 740 (34), 710 (34), 710 (29), 675 (45).

Delcosine Perchlorate

The salt was recrystallized, m.p. 217–218°, and reanalyzed. Found: C, 51.90, 52.10; H, 6.94, 7.16; N, 2.45. Calc. for $C_{24}H_{39}O_7N \cdot HClO_4$: C, 52.04; H, 7.28; N, 2.53%.

[4]*All melting points are corrected.*

[5]*The infrared spectra were determined on a Perkin–Elmer double beam spectrophotometer model 21. The peaks are indicated by a wave number and the percentage absorption is given by the number in parentheses. Shoulders are indicated by an S after the wave number. Unless otherwise indicated the compounds were suspended in nujol as mulls for the determination.*

Delcosine Hydriodide

Delcosine was neutralized with hydriodic acid and the solution evaporated to dryness. The residue was crystallized twice from methanol. Delcosine hydriodide melted at 196–197°. Found: C, 49.39; H, 6.84; N, 2.27; I, 21.64. Calc. for $C_{24}H_{39}O_7N \cdot HI$: C, 49.61; H, 6.94; N, 2.41; I, 21.83%. All attempts to prepare delcosine methiodide failed and invariably gave rise to the hydriodide.

Delcosine Bitartrate

The salt was prepared by mixing equivalent quantities of the base and tartaric acid. After recrystallization it melted at 165–166°. Found: C, 55.55, 55.80; H, 7.03, 7.26; N, 2.47. Calc. for $C_{24}H_{39}O_7N \cdot C_4H_6O_6$: C, 55.71; H, 7.51; N, 2.32%.

Monoacetyldelcosine

Delcosine (260 mgm.) was heated for three hours at 80–90° with acetic acid (3.0 ml.) and trifluoroacetic acid (0.10 ml.). Ethanol (2 ml.) was then added and the solution alkalized with 4% aqueous sodium carbonate. The resulting solution was extracted with chloroform and the combined extract dried and evaporated under reduced pressure. The residue (288 mgm.) was dissolved in ether (5 ml.) containing ethanol (0.5 ml.) and the solution diluted with petroleum ether. The monoacetyldelcosine which crystallized out was sublimed at 182° at 10^{-5} mm., and recrystallized twice from ether – petroleum ether from which it separated as colorless prisms, m.p. 191–193°, wt. 225 mgm. $[\alpha]_D^{28}+32$ (*c*, 3.17 in chloroform). Found: C, 63.09, 63.44; H, 8.27, 8.49; N, 2.82, 2.70; OCH_3, 18.75; act. H (Zerewitinow), 0.51; mol. wt. (titration) 495.5. Calc. for $C_{24}H_{38}O_7N \cdot COCH_3$: C, 63.01; H, 8.34; N, 2.83; 3 OCH_3, 18.79; 3 act. H, 0.61%; mol. wt. 495.6. The pK value was 6.25 (value of pH at half titration in 50% methanol with 0.0333 *N* hydrochloric acid).

In admixture with Goodson's "alkaloid B" (m.p. 193–195°, $[\alpha]_D+34°$), the melting point of monoacetyldelcosine was unchanged. The infrared absorption spectra of the two bases taken in carbon disulphide solution were superimposable. They contained the following peaks: 3520 (45), 3475 (76), 3210 (35), 2940 (88), 2880 (81), 1735 (95), 1385 (76), 1365 (77), 1337S (50), 1325 (65), 1300 (65), 1245 (98), 1225 (88), 1215S (84), 1190 (75), 1170 (69), 1135S (78), 1120 (92), 1100 (98), 1087 (99), 1050 (82), 1040 (78), 1030 (64), 1015 (59), 1000 (58), 985 (43), 970 (47), 955 (53), 940 (48), 910 (37), 810 (16), 760 (32), 740 (34), 720 (29), 685 (39), 660 (47), 635 (36).

Monoacetyldelcosine was also obtained by the action of acetyl chloride on delcosine at room temperature for five minutes.

Mono-(trichloroacetyl)-delcosine

Delcosine (191 mgm.) was kept at 75° for five hours with trichloroacetic acid (3.2 gm.) and trifluoroacetic acid (0.1 ml.). The product was worked up as described for monoacetyldelcosine except that it could not be sublimed. After several recrystallizations from alcohol–water, mono-(trichloroacetyl)-delcosine melted at 172.5–173.5° (wt. 125 mgm.). Found: C, 53.50, 53.41;

H, 6.47, 6.42; N, 2.56%. Calc. for $C_{24}H_{38}O_7N \cdot COCCl_3$: C, 52.13; H, 6.40; N, 2.34%.

Diacetyldelcosine

Delcosine (338 mgm.) was dissolved in dry pyridine (3.0 ml.) and freshly distilled acetic anhydride (2.0 ml.) added to the solution which was kept at 87° for eight hours. The colorless reaction mixture was concentrated under reduced pressure to a thick oil to which ethanol (1.5 ml.) and water (3.0 ml.) were added. The basicity of the solution was adjusted to pH 9 to 10 by the addition of 4% aqueous sodium carbonate. A white amorphous precipitate separated and the mixture was extracted with chloroform. The combined extract was evaporated to dryness under reduced pressure and the residual colorless oil (wt. 351 mgm.) dissolved in ethanol. Addition of water to the solution caused the separation of an oil which crystallized on standing overnight, wt. 320 mgm. After two recrystallizations from dilute ethanol diacetyldelcosine consisted of colorless needles, m.p. 127–128°. It was sublimed (140° at 10^{-4} mm.) without decomposition. pK, 5.33 (pH at half titration in 50% methanol). Found: C, 62.49, 62.76; H, 7.99, 8.08; N, 2.89, 2.76; OCH_3, 17.14, 17.11; act. H (Zerewitinow), 0.36%; mol. wt. (titration), 536. Calc. for $C_{24}H_{37}O_7N \cdot (COCH_3)_2$: C, 62.55; H, 8.06; N, 2.61; 3 OCH_3, 17.32; 2 act. H, 0.37%; mol. wt. 537.6. The infrared absorption spectrum contained two absorption bands at 3459 $cm.^{-1}$ and 3392 $cm.^{-1}$ indicative of two unreacted hydroxyl groups. It also contained a strong carbonyl band at 1730 $cm.^{-1}$ and an ester band at 1246 cm^{-1}.

Dipropionyldelcosine

Delcosine (186 mgm.) was added to dry pyridine (4.0 ml.) and propionic anhydride (1.0 ml.), and the mixture heated for three hours at 100°. The dipropionyldelcosine was isolated exactly as described for diacetyldelcosine, and after several recrystallizations dilute ethanol melted at 119–120°. It could be sublimed (147° at 10^{-5}mm.) without decomposition. Found: C, 63.88; H, 8.46; N, 2.58. Calc. for $C_{24}H_{37}O_7N \cdot (COC_2H_5)_2$: C, 63.69; H, 8.37, N, 2.48%. The infrared spectrum of this derivative contained two absorption bands at 3480 $cm.^{-1}$ and 3418 $cm.^{-1}$ in the OH region, a carbonyl band at 1732 $cm.^{-1}$ and a strong absorption peak at 1190 $cm.^{-1}$ attributable to the ester groups.

Further Acetylation Experiments

A mixture of delcosine (427 mgm.) and purified acetyl chloride (5 ml.) was kept at room temperature for 72 hr. The excess reagent was distilled off under reduced pressure and the oily residue dissolved in dilute ethanol. The solution was alkalized to pH 10 with 4% aqueous sodium carbonate and extracted with chloroform. Addition of ether to the chloroform brought down a crystalline precipitate which was filtered, m.p. 264–266°. Further additions of ether caused the precipitation of a second substance, which after two crystallizations from alcohol–ether proved to be monoacetyldelcosine, m.p. 186–189°, wt. 220 mgm. The higher melting product was recrystallized from alcohol–ether

from which it was obtained as colorless needles, m.p. 268.5–269.5°. The infrared absorption spectrum showed no absorption in the OH region. Found: C, 61.33, 61.39; H, 7.38, 7.11; N, 2.51; OCH_3, 16.01. Calc. for $C_{24}H_{35}O_7N \cdot (COCH_3)_4$: C, 61.82; H, 7.62; N, 2.25; 3 OCH_3, 14.98%.

Delcosine (825 mgm.) and excess acetyl chloride (5 ml.) were maintained at 60° for four hours. The excess acetyl chloride was evaporated under diminished pressure, the residue dissolved in water, the solution alkalized with sodium carbonate, and extracted with chloroform. The residue left after evaporation of the chloroform was crystallized from methanol from which it separated in colorless needles, m.p. 159–161°, either alone or in admixture with the derivative of similar melting point reported by Marion and Edwards (4), $[\alpha]_D^{28}+31°$ (*c*, 2.92 in chloroform), yield 310 mgm. The mother liquors yielded a further 100 mgm. of the same derivative. A sample for analysis was dried for 12 hr. at 92° at 0.1 mm. Found: C, 64.82, 64.73; H, 7.85, 7.87; act. H, nil. Calc. for $C_{28}H_{41}O_8N$: C, 64.72; H, 7.95%. The infrared absorption spectrum of the substances showed no absorption in the OH region.

From some preparations of the foregoing derivative, small quantities of a crystalline substance could be obtained which was characterized by its relative insolubility in methanol. Through this property it could be purified readily and crystallized as needles, m.p. 204°, either alone or in admixture with the "triacetyldelcosine" of Marion and Edwards (4). On the basis of the new formula this corresponds to a diacetyldelcosine, $[\alpha]_D^{28}+7.5°$ (*c*, 1.6 in chloroform). For analysis a sample was dried for 36 hr. at 100° at 0.1 mm. Found: C, 62.62, 62.42; H, 7.66, 7.99; OCH_3, 17.7; act. H (Zerewitinow), 0.41, 0.39%. Calc. for $C_{24}H_{37}O_7N(COCH_3)_2$: C, 62.55; H, 8.06; 3 OCH_3, 17.32; 2 act. H, 0.37%. This diacetyldelcosine was not identical with that described above (m.p. 127–128°) and the infrared absorption spectra of both compounds show quite pronounced differences.

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SOME REACTIONS OF ETHYL 2-PYRIDINEACETATE 1,2-DICARBETHOXY-3-OXO-OCTAHYDROPYRROCOLINE[1]

By O. E. Edwards, M. Chaput[2], F. H. Clarke[3], and Tara Singh[4]

ABSTRACT

Ethyl α-acetoxy-2-pyridineacetate and ethyl α-bromo-2-pyridineacetate have been prepared, and the latter converted in three steps to 1,2-dicarbethoxy-3-oxo-octahydropyrrocoline. The main carbonyl band of simple saturated five membered lactams in the infrared is observed to lie close to 1700 cm^{-1}.

The methylene group of ethyl 2-pyridineacetate is of comparable activity to that of ethyl acetoacetate. For example, a useful anion can be obtained by reaction with sodium or potassium (1, 4). Further parallel between the reactivities of the two compounds has now been found in the ease of bromination and acetoxylation. Like acetoacetic ester (6), 2-pyridineacetic esters react rapidly with a molar equivalent of bromine at 5°C. in carbon disulphide solution to give α-bromo esters, and react at room temperature with lead tetraacetate in benzene to give the α-acetoxy compound. In contrast, the methylene group of malonic esters does not react at a useful rate with lead tetraacetate in benzene until the solution is heated to around 100° (6).

The synthesis of octahydropyrrocolines with reactive substituents has been achieved by Clemo and co-workers (2, 3, 4) and by Lions and Willison (10). The work of Diels and co-workers (5, and earlier papers) has led to pyrrocolines substituted with carboxyls, which presumably could be reduced to the corresponding octahydro derivatives. By reaction of ethyl α-bromo-2-pyridineacetate with the anion from ethyl malonate, reduction of the product, and cyclization, 1,2-dicarbethoxy-3-oxo-octahydropyrrocoline III has now been obtained. The malonic hydrogen and carboxyl groups in this compound are of potential value for building additional rings on the five membered ring.

The reactions used in preparing and characterizing the various products are shown in the flowsheet. The mixture obtained when the bromo compound reacted with the malonic anion contained some ethyl 1,1,2,2-ethanetetracarboxylate, probably arising from ethyl bromomalonate formed by bromine exchange. This could be partly removed by distillation under high vacuum, but the desired product I could not be distilled without considerable decomposition. By chromatography on neutral alumina, however, I could be freed from the ethanetetracarboxylic ester, unchanged malonic ester, and colored impurities.

I proved to be a very weak base (pK_A around 2.4 in 50% aqueous methanol). A somewhat low basicity (pK 3.6) has been observed for α,α-di-(2-pyridyl)-

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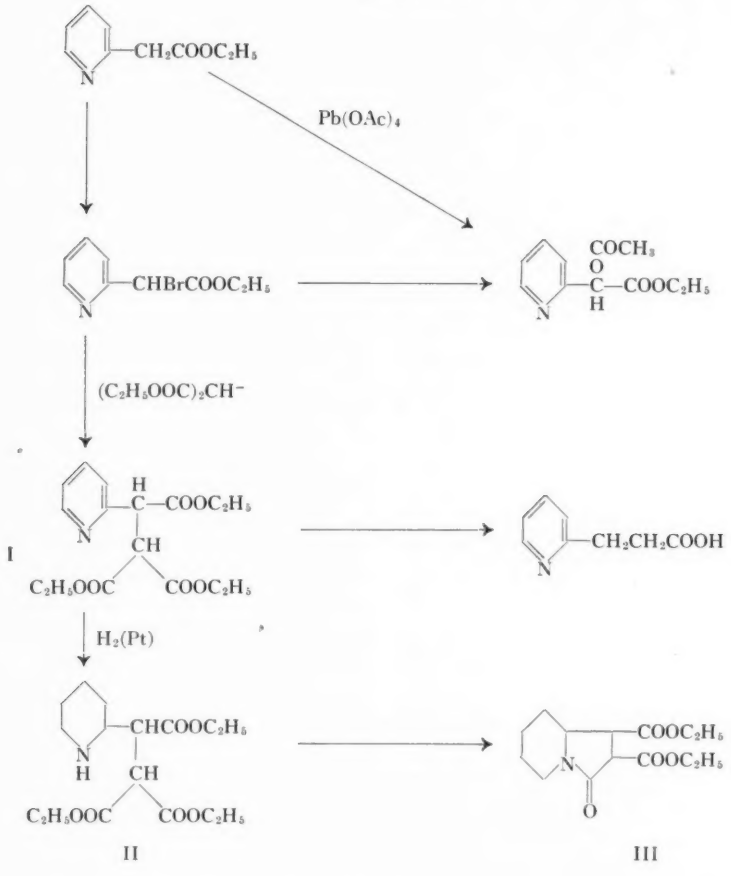
FLOWSHEET



γ,γ-dicarbethoxypropane (9). This may in part be due to interaction across space between the nitrogen and the ester carbonyls. In the case of I, however, the inductive effect of the three carbethoxy groups must be the main cause of the low basicity. The ultraviolet spectrum of I (λ_{max} 261mμ, log ε 3.54) was very similar to that of α-picoline, hence no rearrangement of the double bonds had taken place.

Attempts to prepare ethyl α–β-di(2-pyridyl)-succinate by reaction of ethyl α-bromo-2-pyridineacetate and the anion from ethyl pyridineacetate gave intractable highly colored products. Similar results were obtained in an attempt to obtain this compound by coupling two molecules of the anion using iodine.

When the crude I was hydrolyzed and decarboxylated, considerable tar was produced, but a 27% yield of β-(2-pyridyl)-propionic acid was obtained.

The piperidine triester II underwent smooth cyclization when distillation was attempted and only the lactam III was obtained. When III was hydrolyzed, the mixture of stereoisomeric acids proved reluctant to crystallize. On long standing, however, two diastereoisomers melting with decomposition near 170° were obtained in poor yield.

The C=O stretching vibration in saturated N-alkyl six membered lactams gives rise to an absorption band near 1640 cm.$^{-1}$ (8). The position of this band for four pyrrolidones is indicated in Table I. From these observations it appears

TABLE I

Compound	Wave number, cm.$^{-1}$	State
Lactam III	1705	Liquid film
	1690	Chloroform solution
N-methyl-2-pyrrolidone	1690	Liquid film
	1680	Chloroform solution
Octahydrogelsemine*	1693	Nujol mull
2-Pyrrolidone	1695	Film from melt

**The authors wish to thank Dr. L. Marion for permission to use this value.*

that in simple saturated systems the position of this band can be used to assign ring size to a lactam. The spectrum of the 3-oxo-octahydropyrrocolinedicarboxylic acid, however, had unusual absorption in the 6 μ region, and the bands cannot be assigned to any individual vibration.

It is interesting to note that the relatively intense band in the OH, NH stretching region (around 3450 cm.$^{-1}$) which has been observed for N-alkyl six membered lactams (8) also appears in the spectra of the N-substituted five membered lactams. In a recent paper (11) this band has been attributed to water in the samples. We consider this unlikely in our own cases in view of the high distillation temperatures (center cuts were taken), the good carbon, hydrogen analyses of the compounds, and the complete disappearance of the bands in chloroform solution. Hence, unless some very unusual spectral effect gives rise to this band, it seems likely that it is due to the presence of considerable enol in the liquid state.

EXPERIMENTAL

The infrared spectra were taken on a Perkin-Elmer model 21 double beam spectrophotometer with a sodium chloride prism. The location of the bands is given in cm.$^{-1}$ followed in brackets by the percentage absorption. The ultraviolet spectra were taken using a Beckmann D.U. spectrophotometer.

Methyl α-Bromo-2-pyridineacetate

Methyl 2-pyridineacetate (2.0 gm., b.p. 90°, 2 mm.) was dissolved in carbon disulphide in a flask surrounded by cracked ice. A solution of 2.2 gm. of bromine in 10 ml. of carbon disulphide was added slowly while the reaction mixture was

stirred. After the addition the reaction mixture was allowed to stand at room temperature for one hour. The carbon disulphide was boiled off and the residue covered with a layer of ether. Excess saturated potassium carbonate solution was added, the ether layer separated, and the aqueous layer extracted three times with ether. The yellow oil recovered from the dried ether solution was distilled over a short path at a bath temperature of 90°, 0.2 mm. Yield, 2.3 gm. Found: C, 41.78; H, 3.32; N, 5.69. Calc. for $C_8H_8O_2NBr$: C, 41.76; H, 3.51; N, 6.09.

Ethyl α-Bromo-2-pyridineacetate

Prepared as described for the methyl ester in 77% yield. Distilled over a short path at a bath temperature of 90°, 0.2 mm. Found: Br, 31.76, 31.12. Calc. for $C_9H_{10}O_2NBr$: Br, 32.74. The compound is sensitive, and develops color on heating or keeping, hence the somewhat low bromine values.

Ethyl α-(Dicarbethoxymethyl)-2-pyridineacetate (I)

To ethyl α-bromo-2-pyridineacetate (2.75 gm.) in 10 ml. of absolute ethanol was added dropwise a solution of sodio–malonic ester (from 0.265 gm. of sodium and 1.80 gm. of ethyl malonate) in 5 cc. of ethanol. After the addition the mixture was allowed to sit for 0.5 hr. at room temperature. The ethanol was then removed under reduced pressure. The residue was taken up in methylene chloride, and this solution extracted three times with 3 *N* hydrochloric acid (40 cc.). The methylene chloride solution contained 2.8 gm. of oil. The aqueous solution was made alkaline with ammonia and extracted with methylene chloride giving 0.91 gm. of base.

The neutral oil was chromatographed on 56 gm. of neutral alumina (activity 2–3, Brockmann scale). Three hundred cubic centimeters of benzene eluted 2.38 gm. of pale reddish oil. The remaining esters were eluted with chloroform and ethanol in chloroform (304 mgm.). The benzene eluates were rechromatographed on 51 gm. of neutral alumina activity 1–2. The first three groups of eluates were colorless oils. Fraction 1 contained some ethyl malonate, and

Solvent	Volume, cc.	Weight eluted, mgm.	λ_{max} in mμ	ϵ_{max}
1. 50% Petroleum ether – benzene	400	876	260.5	1690
2. Benzene	250	489	260.5	3420
3. 50% Chloroform benzene	200	276	260.5	3470
4. Chloroform and ethanol in chloroform	400	490	Not determined	

ethyl 1,1,2,2-ethanetetracarboxylate in addition to the desired product. The first two esters could be separated by distillation under high vacuum. The distillate crystallized. After recrystallization from ether petroleum ether it

melted at 76° (1,1,2,2-ethanetetracarboxylate melts at 76°). Found: C, 52.84; H, 6.93. Calc. for $C_{14}H_{22}O_8$: C, 52.82; H, 6.97.

Fraction 3 in 0.01 *N* hydrochloric acid in ethanol had λ_{max} 262 mμ, log ε 3.78. It had a pK_A of 2.4 in 50% aqueous methanol.

Distillation of a sample of fraction 3 under 5×10^{-5} mm. and a bath temperature of 110° gave an orange oil, and left a tarry residue. The distillate was analyzed. Found: C, 58.00; H, 6.71. Calc. for $C_{16}H_{21}O_6N$: C, 59.43; H, 6.55.

Hydrolysis and Decarboxylation of I

Four grams of crude I was hydrolyzed with hot dilute sodium hydroxide solution. The solution was made just acid to Congo red paper with hydrochloric acid. The water was removed under reduced pressure and the residue extracted with ethanol. This was transferred to a bulb and heated under 0.2 mm. pressure. At 120° brisk decomposition took place. The product was then sublimed under 3×10^{-3} mm. pressure, giving 520 mgm. of crystalline solid. This was suspended in hot benzene and filtered. The crystals melted at 141° (β-(2-pyridyl)-propionic acid is reported to melt at 141° (7)). Found: C, 63.38; H, 5.79. Calc. for $C_8H_9O_2N$: C, 63.56; H, 6.00.

1,2-Dicarbethoxy-3-oxo-octahydropyrrocoline

A sample of I, calculated from the ultraviolet spectrum to contain 1.2 gm. of the triester, was dissolved in 15 ml. of ethanol containing 0.5 ml. of concentrated hydrochloric acid. In the presence of platinum from 0.16 gm. of platinum oxide this absorbed 260 ml. of hydrogen at 25°C. in 35 min. (2.9 moles per mole). After removal of the catalyst and ethanol, the product was dissolved in dilute acid and the neutral impurity extracted with ether. The acid solution was made basic with sodium carbonate and the base extracted with methylene chloride giving 960 mgm. of colorless oil. No crystalline picrate of this base could be obtained. On treatment with acetic anhydride at room temperature a sample of the base gave a neutral oil. When the base was distilled under 10^{-3} mm. at a bath temperature of 120°, a neutral oil resulted which analyzed correctly for the pyrrocolone. Found: C, 59.75; H, 7.56. The distillate was dissolved in methylene chloride, washed with acid and alkali, dried, and the oil redistilled. Found: C, 59.78, 59.20; H, 7.50, 7.31. Calc. for $C_{14}H_{21}O_5N$: C, 59.33; H, 7.49. Infrared spectrum (liquid film): 3450 (12), 2960 (56), 2880 (35), 1740 (93), 1705 (94), 1452 (67), 1435 (62), 1404 (49), 1375 (63), 1315 (58), 1263 (83), 1237 (79), 1215 (80), 1180 (78), 1117 (38), 1097 (40), 1030 (66), 972 (27), 949 (21), 915 (11), 885 (18), 855 (32), 700 (27).

1,2-Dicarboxy-3-oxo-octahydropyrrocoline

A solution of 0.98 gm. of base from the hydrogenation of I was saponified overnight with sodium hydroxide in aqueous ethanol. The solution was made just acid to Congo red paper with hydrochloric acid, then evaporated to dryness under reduced pressure. No amino acid could be extracted from this residue by boiling chloroform. The salts were dissolved in 6 *N* hydrochloric acid, then the solution taken to dryness. The residue was taken up in water

and again taken to dryness under reduced pressure. The solid was extracted with cold dry ethanol, giving 0.73 gm. of viscous oil. This was readily soluble in chloroform. When a concentrated chloroform–ether solution of this acid stood for several weeks a crystalline compound (40 mgm.) separated. After two recrystallizations from acetone ether this gave 10 mgm. m.p. 175° dec. neutral equivalent: 107. Calc. for $C_{10}H_{13}O_5N$, neutral equivalent 113.6. On long standing the main mother liquor deposited a second crop of crystals. After recrystallization 60 mgm. was obtained, m.p. 171° dec. When mixed with the first crop this melted at 165° dec. Found: neutral equivalent, 126; C, 53.18; H, 5.69; N, 6.38. Calc. for $C_{10}H_{13}O_5N$: C, 52.86; H, 5.77; N, 6.17, neutral equivalent, 113.6. The pK_A's of the two carboxyl groups were approximately 4.1 and 5.7 in 50% aqueous methanol.

Ethyl α-Acetoxy-2-pyridineacetate

(*a*) Ethyl α-bromo-2-pyridineacetate (1.13 gm.) was added to a solution of 4.0 gm. of sodium acetate in 20 cc. of ethanol and 1 cc. of water. The mixture was refluxed for six hours, the solvent then removed under reduced pressure, and the residue extracted with ether. The 715 mgm. of oil recovered from the ether was distilled at a bath temperature of 97° under 0.2 mm. pressure giving 490 mgm. of nearly colorless oil. Found: C, 59.20; H, 5.63. Calc. for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87. Infrared spectrum (liquid film) 3480 (6), 3080 (16), 3000 (37), 1750 (93), 1600 (65), 1580 (45), 1479 (56), 1443 (65), 1376 (75), 1342 (46), 1235 (83), 1216 (91), 1187 (80), 1099 (53), 957 (27), 925 (26), 830 (18), 754 (57), 699 (29), 649 (25).

The base, probably because of its low basicity, formed a picrate which had more of the character of a molecular complex than that of a salt. It was quite soluble in ether, and it had to be crystallized from a concentrated solution in this solvent. It melted at 100°. Found: C, 45.22, 45.53; H, 3.55, 3.65. Calc. for $C_{17}H_{16}N_4O_{11}$, C, 45.14; H, 3.57.

(*b*) Ethyl 2-pyridineacetate (2.0 gm.) was added to a solution of 4 gm. of lead tetraacetate in 30 cc. of benzene. Some heat was evolved, the solution turned brown, and a crystalline precipitate settled. After one hour at room temperature the mixture was filtered and the solid washed with benzene. The benzene solution was washed with sodium bicarbonate solution, dried, and distilled. A residue of 1.6 gm. of dark liquid remained. This was distilled over a short path at a bath temperature of 85–120° under 0.3 mm. pressure. The 600 mgm. of brown distillate was redistilled, giving 450 mgm. of faintly colored oil. The infrared spectrum of this was identical to that of the product from (*a*).

1-Methyl-2-pyrrolidone[5]

This was distilled under one atmosphere pressure (b.p. 200°), a center cut being taken for the spectra. Calc. for C_5H_9ON: C, 60.58; H, 9.15. Found: C, 60.90; H, 9.24. Infrared spectrum: (*a*) Liquid film, 3480 (34), 2950 (39), 2900 (38), 1690 (92), 1508 (48), 1479 (40), 1465 (42), 1442 (45), 1432 (48), 1407 (55), 1303 (67), 1267 (45), 1230 (18), 1173 (13), 1114 (36), 1025 (10), 985 (25), 925 (11), 847 (11), 740 (13), 650 (34). (*b*) Chloroform solution 31

mgm. per ml.; 3020 (66), 2900 (33), 1680 (97), 1508 (51), 1479 (37), 1465 (36), 1446 (40), 1432 (44), 1410 (59), 1305 (67), 1266 (43), 1210 (67), 1175 (14), 1115 (33), 1025 (9), 985 (22).

2-Pyrrolidone[5]

[5]*The authors wish to thank the General Aniline and Film Corporation for generous gifts of these compounds.*

Melting point 25°. For the spectrum, a crystal was melted between rock salt plates. Infrared spectrum: 3260 (49), 2980 (29), 2910 (30), 1695 (89), 1500 (20), 1470 (31), 1445 (27), 1431 (30), 1385 (18), 1290 (50), 1272 (40), 1230 (12), 1170 (10), 1070 (21), 996 (22), 916 (7), 885 (9), 680 (32).

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THE C^{14} ISOTOPE EFFECT IN THE CONDENSATION OF BENZOYLBENZOIC ACID-CARBOXYL-C^{14} TO ANTHRAQUINONE-9-C^{14} [1]

By W. H. Stevens and D. A. Crowder

ABSTRACT

Benzoylbenzoic acid-carboxyl-C^{14} has been synthesized. The C^{14} isotope effect in the condensation of this acid to anthraquinone-9-C^{14} in concentrated sulphuric acid has been measured and the ratio of the reaction rates, $k(14)/k(12)$, found to be 1.074 ± 0.003. It is suggested that this result supports the mechanism for this reaction proposed by Newman.

INTRODUCTION

A simplified theoretical treatment of isotope effects on reaction rates has been given by Bigeleisen (3). He predicts that substitution of a heavier isotopic atom in a given molecular species will generally cause the reaction rate constant for that species to decrease. This might be termed the "normal" isotope effect. The Bigeleisen treatment also gives the theoretical conditions which must obtain in a reaction for a "reverse"[2] isotope effect to occur. It appears that these conditions are most likely to be satisfied in reactions where bond formation is the rate controlling step.

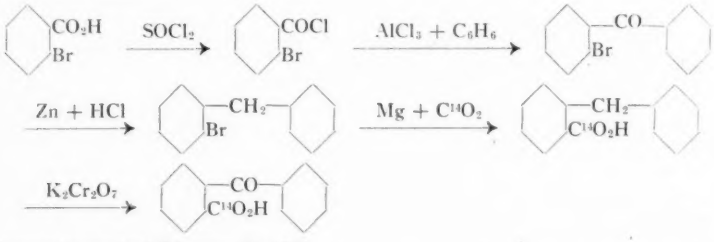
In almost all of the reactions in which carbon isotope effects have been found to occur thus far, bond cleavage is the rate controlling step. In these reactions the isotope effect is "normal", with the exception of the iodination of acetone (12). An explanation of the reverse isotope effect found in this reaction has been given by Yankwich (18). A reverse nitrogen isotope effect has been observed in the deammonation of phthalamide (15).

We were led to investigate the C^{14} isotope effect in the condensation of *o*-benzoylbenzoic acid-carboxyl-C^{14} to anthraquinone-9-C^{14} because it appeared that carbon to carbon bond formation could be the rate controlling step in the reaction. This paper reports a "reverse" isotope effect in this reaction and discusses how this result supports the mechanism proposed for the reaction by Newman (10).

EXPERIMENTAL

A. *Preparation of o-Benzoylbenzoic Acid-carboxyl-C^{14}*

o-Benzoylbenzoic acid-carboxyl-C^{14} was synthesized using the following sequence of reactions:



[1] *Manuscript received February 19, 1954.*
Contribution from: Chemistry Branch, Atomic Energy of Canada Limited, Chalk River, Ontario. Issued as A.E.C.L. No. 118.
[2] *I.e. for the heavier isotopic molecule to have the greater rate constant.*

o-Bromobenzophenone was prepared according to the method given by Bergman (2). *o*-Bromodiphenyl methane was obtained by a Clemmenson reduction of this ketone following the method of Clarkson and Gomberg (6). Benzylbenzoic acid-carboxyl-C^{14} was prepared by carbonating the Grignard made from the *o*-bromodiphenylmethane on a 5 mM. scale using a vacuum line technique which has been described earlier (16). The benzylbenzoic acid-carboxyl-C^{14} was oxidized to benzoylbenzoic acid-carboxyl-C^{14} using potassium dichromate in acetic acid. This acid was diluted with several times its weight of inactive *o*-benzoylbenzoic acid and recrystallized from 15% aqueous alcohol, m.p. 127°C.

B. *The Condensation Reaction*

The condensation of *o*-benzoylbenzoic acid to anthraquinone in concentrated sulphuric acid was found to be a first order reaction by Gleason and Dougherty (8).

The experimental procedure used for our work was as follows: A sample of *o*-benzoylbenzoic acid-carboxyl-C^{14}, approximately 3.5 gm., was accurately weighed into a dry 50 ml. glass stoppered erlenmeyer flask. Concentrated sulphuric acid (25 ml.) was added and the flask reweighed. After the organic acid was completely dissolved, a 10 ml. sample of the homogeneous solution was withdrawn and run into a dry weighed glass stoppered tube. The tube and contents were weighed and placed in a thermostated water bath at 80 ± 0.5°C. for 15 min. This temperature and time of reaction were known to give about 10% reaction. The sulphuric acid solution was then poured onto approximately 50 gm. of crushed ice, and the tube was thoroughly rinsed out with cold water. The mixture was digested on a hot water bath for a half hour, and the precipitated anthraquinone filtered into a weighed sintered glass gooch crucible and washed with dilute ammonia solution and water. The crucible and contents were dried in a vacuum desiccator over concentrated sulphuric acid and then weighed. The extent of the reaction was calculated from the known weights.

A second 10 ml. sample of the sulphuric acid solution of *o*-benzoylbenzoic acid-carboxyl-C^{14} was withdrawn, heated, and treated in the same manner to give a second sample of anthraquinone-9-C^{14}.

The flask with the residual sulphuric acid solution (approximately 5 ml.) was heated at 100°C. for three hours, which converted the remaining *o*-benzoylbenzoic acid-carboxyl-C^{14} practically quantitatively into anthraquinone-9-C^{14}.

The entire procedure was repeated to give three more samples of anthraquinone-9-C^{14}, two from partially reacted *o*-benzoylbenzoic acid-carboxyl-C^{14} and one from completely reacted *o*-benzoylbenzoic acid-carboxyl-C^{14}.

The remaining *o*-benzoylbenzoic acid-carboxyl-C^{14}, about 0.5 gm., was heated in 5 ml. of concentrated sulphuric acid for five hours and the anthraquinone-9-C^{14} isolated in the usual manner to give a third sample of anthraquinone-9-C^{14} from completely reacted *o*-benzoylbenzoic acid-carboxyl-C^{14}.

All samples of anthraquinone-9-C^{14} were recrystallized from absolute ethanol and vacuum dried before radioactivity measurements were made.

In most previous work on C^{14} isotope effects in this laboratory (5, 16, 17) relative specific activities have been determined by comparing the counting rates of uniform, extremely thin samples of labeled compounds prepared by evaporation of known amounts of appropriate solutions on stainless steel trays. This technique did not give the desired reproducibility with anthraquinone-9-C^{14}. An adaptation of a method recently described by Schwebel, Isbell, and Karabinos (14) was then used with very satisfactory results. Briefly, the method consists of dissolving a labeled compound in a suitable, relatively nonvolatile solvent and using a thick layer of solution, i.e. a layer thicker than 25 mgm./cm.^{2}, as a sample for counting in a gas-flow proportional counter.

The technique we adopted was as follows: an approximately 20.0 mgm. sample of an anthraquinone-9-C^{14} sample was accurately weighed (± 0.02 mgm.) into a 2 ml. glass-stoppered volumetric tube. Concentrated sulphuric acid was added to give 2 ml. of solution. A 200 λ sample of this sulphuric acid solution was pipetted into a stainless steel dish and the dish rapidly transferred to a methane-flow proportional counter shown in Fig. 1. Five such samples were counted for each solution and two different sulphuric acid solutions were made up from each original anthraquinone-9-C^{14} sample.

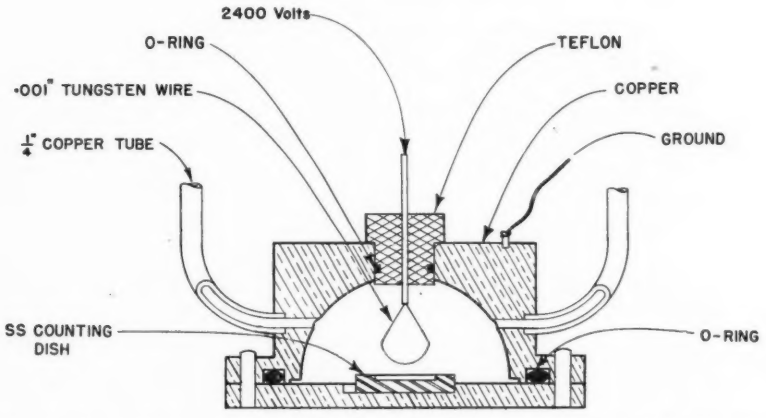


FIG. 1. Sectional view of methane-flow proportional counter and sample dish assembly.

Initially, it was found that a sample counting rate gradually decreased as a sample was counted over a period of an hour. This was found to be caused by some component of the commercial methane (96% methane) dissolving in the concentrated sulphuric acid solution. The difficulty was overcome by scrubbing the methane with concentrated sulphuric acid before it entered the counter.

This thick layer solution counting technique has the advantage, compared with either thick or thin solid sample counting, that counting samples are more reproducible. This is because a uniformly smooth layer, the entire area of

which is "infinitely thick"[3] for C^{14} β particles, is presented to the counter. For a given area of sample, the measured C^{14} activity for any solution is volume independent, i.e. is independent of the thickness, provided the thickness is greater than 25 mgm./cm.^{2}, and is directly proportional to the concentration of dissolved labeled compound within comparatively wide limits.

RESULTS

Stevens and Attree (17) derived the equation

$$k(14)/k(12) = \ln (1 - rf)/(1 - f)$$

to express the C^{14} isotope effect in a given reaction, quantitatively. In this equation, $k(14)/k(12)$ is the ratio of the reaction rate constant of the C^{14} labeled compound to the reaction rate constant of the unlabeled compound, f is the fraction of initial compound reacted, and r is the ratio of the specific activity of the accumulated product, after fraction f has reacted, to the specific activity of the product after complete reaction. This equation has been used to calculate the C^{14} isotope effect in the present reaction.

The experimental results and calculated isotope effect are summarized in Table I. The "relative specific activities" given are the activities of the

TABLE I

EXPERIMENTAL RESULTS

Anthraquinone-9-C^{14} sample No.	Fraction reacted (f)	Relative specific activities (counts/min.)	Specific activity ratio (r)	$k(14)/k(12)$ $\ln (1-rf)/\ln (r-f)$
1 T	Reaction	4716 ± 43		
2 T	taken to	4700 ± 42		
3 T	completion	4766 ± 49		
Average		4727 ± 28		
1 P–1	0.123	5058 ± 33	1.070	1.076
1 P–2	0.119	5048 ± 34	1.067	1.072
2 P–1	0.124	5090 ± 51	1.076	1.073
2 P–2	0.111	5054 ± 22	1.069	1.074
Average				1.074 ± .003

concentrated sulphuric acid solutions, measured under our standard conditions, normalized to a standard concentration of 10 mgm. of anthraquinone-9-C^{14} per ml. of solution. Each value is the average for ten separate counting samples, five from each of two separate sulphuric acid solutions. The standard deviation in the counting rate is shown in each case.

The specific activity ratios were calculated using the average specific activity value for the three complete reaction samples as denominator.

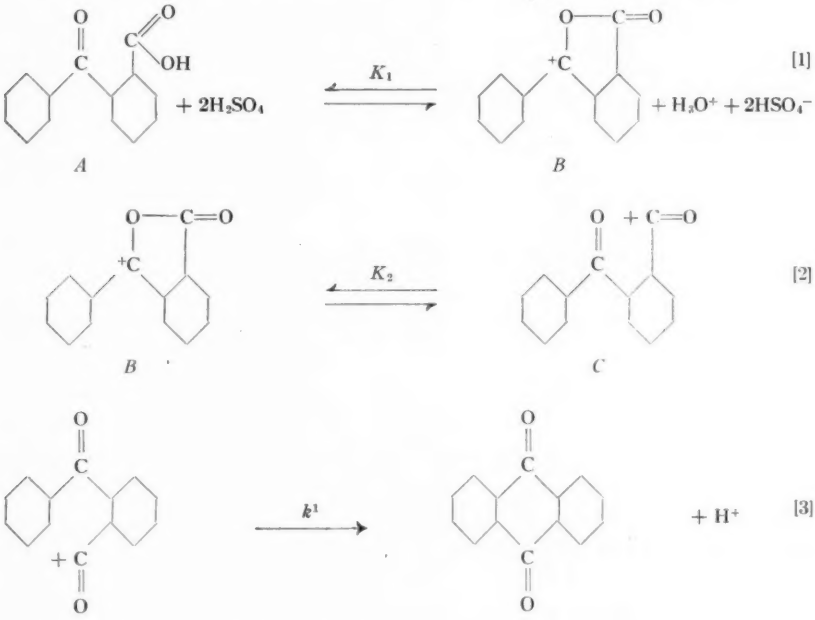
[3] *A thickness such that all β particles originating at the bottom of the sample layer are completely absorbed by the overlaying sample itself. The sample thus exhibits saturation activity. For C^{14}, this thickness is not greater than 25 mgm./cm.^{2}*

The limit given for the average value of $k(14)/k(12)$ is the probable error calculated directly from the four separate values obtained.

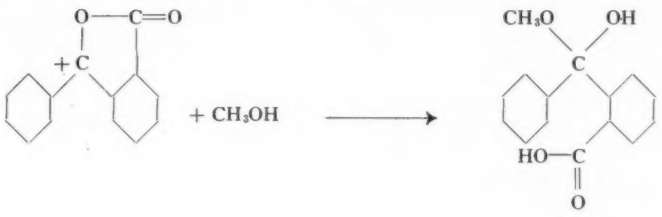
Sources of Error.—The values for $k(14)/k(12)$ are rather insensitive to errors in f, when f is approximately 0.1. A 3% error in f, for any sample, would only change the $k(14)/k(12)$ value for that sample by approximately 0.001. As can be seen from Table I, the probable counting errors are below 1%. The greatest source of error would seem to occur in determining the concentration of the sulphuric acid solutions prepared for counting purposes. The weighing errors were negligible at approximately 0.1%, but the limits given by the manufacturer for the volumes of the 2 ml. graduated tubes are ± 0.03 ml., or $1\frac{1}{2}\%$.

DISCUSSION

In 1942, Newman (10) commented: "Although ring closure condensations with acids of the *o*-benzylbenzoic and γ-arylbutyric type take place fairly readily in sulphuric acid, anthraquinone formation remains a reaction unique in organic chemistry. The ease and high yield with which this condensation takes place ortho to a ketonic function are indeed remarkable". He proposed the following mechanism for the reaction:



His evidence for the equilibrium in reaction [1] was the fact that after a solution of *o*-benzoylbenzoic acid in cold concentrated sulphuric acid was poured into methanol, a high yield of the pseudo methyl ester was obtained. This reaction was formulated as:



[4]

Conversely, after a sulphuric acid solution of the pseudo ester was poured into water, a good yield of *o*-benzoylbenzoic acid was obtained. (The true ester was only hydrolyzed to a small extent by this latter treatment.) More recently, Newman (11) measured the freezing point depression of solutions of *o*-benzoylbenzoic acid in concentrated sulphuric acid and found that the van 't Hoff "i factor" is 3.8, thus confirming that a carbonium ion is formed in sulphuric acid and also indicating that the equilibrium position in reaction [1] lies far to the right.

Newman's argument for reaction [2] was that ring closure would be a very unlikely reaction for the lactone to undergo because of steric factors, and that since anthraquinone is only formed very slowly unless the solution is heated, the lactone ring is very probably broken on heating. There is some evidence for this reaction since Newman found that on heating a pseudo ester with mineral acid, or thionyl chloride, a large fraction isomerizes to the normal ester.

Reaction [3] may be considered as a benzene substitution reaction involving cationoid attack. The carbonyl group would be expected to be meta directing. However, the mesomeric effect of the carbonyl group in this instance may be shared by the two benzene rings, thus lessening its effect on the monosubstituted ring. The steric advantages to ortho substitution may well be then the determining factor in the substitution orientation.

In terms of this mechanism, the reaction rate, v, may be expressed as follows, using square brackets to indicate concentrations.

[1] $$v = k^1 [C]$$

[2] $$= k^1 K_2 [B]$$

[3] $$= k^1 K_1 K_2 [A]$$

The rate constant ratio determined experimentally is in terms of a different rate constant, k, which is defined by the equation

[4] $$v = k\{[A] + [B] + [C]\}$$

[5] $$= k\left\{\frac{[C]}{K_1 K_2} + \frac{[C]}{K_2} + [C]\right\}$$

[6] $$= k[C]\left\{\frac{1}{K_1 K_2} + \frac{1}{K_2} + 1\right\}.$$

From [1] and [6],

$$k^1 = k\left\{\frac{1}{K_1 K_2} + \frac{1}{K_2} + 1\right\}.$$

A much simpler relation between these two rate constants may be obtained by making an approximation. Newman's work indicates that K_1 is large and K_2 small, so that $[A]$ and $[C]$ are both small quantities compared with $[B]$. Equation [4] above may thus be written,

[7] $$v = k\,[B].$$

From [2] and [7], $k = k^1K_2$, and hence, as a good approximation,

$$\frac{k(14)}{k(12)} = \frac{k^1(14)}{k^1(12)} \cdot \frac{K_2(14)}{K_2(12)}.$$

On the basis of the theory of absolute reaction rates developed by Eyring (9), the ratio of the reaction rate constants for two isotopic molecules undergoing a given reaction in the same reaction vessel may be expressed as:

$$\frac{k_1}{k_2} = \frac{\kappa_1}{\kappa_2} \cdot \left(\frac{m_2^*}{m_1^*}\right)^{\frac{1}{2}} \cdot \frac{Q_{A2}}{Q_{A1}} \cdot \frac{Q_1^{\ddagger}}{Q_2^{\ddagger}} \cdot \frac{\delta_2}{\delta_1}.$$

In this equation the κ's are transmission coefficients, the m^*'s are the effective masses of the activated complexes along the coordinate of decomposition, the δ's are the lengths of the tops of the potential energy barriers, and the Q's are complete partition functions. $Q^{\ddagger}$ refers to the activated complex molecules and Q_A to the reactant molecules. The subscripts 1 and 2 refer to the reactions of the two isotopic molecules respectively. The factor m^* is usually calculated as the reduced mass, $mm^1/m + m^1$, of the two atoms involved in the bond being broken or formed in the rate controlling step of the reaction.

Bigeleisen and Mayer (4) have shown that the ratio of the partition functions of two isotopic molecules can be expressed as a simple function of the vibrational energy levels of the molecules. Using various approximations, Bigeleisen (3) obtains the equation

$$\frac{k_1}{k_2} = \left(\frac{m_2^*}{m_1^*}\right)^{\frac{1}{2}} \left(1 + \sum_i^{3N-6} G(u_i)\Delta u_i - \sum_i^{3N^1-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}\right)$$

for the reaction rate constant ratio for isotopic molecules where the Δu's are small. $u = hc\omega/kT$, $\Delta u = hc/kT(\omega_1 - \omega_2)$, and $G(u) = 1/2 - 1/u + 1/(e^u - 1)$. In the derivation of this equation, it is assumed that the effect of isotopic mass on the potential energy surface of the reacting molecules is negligible and that the transmission coefficients, as defined in reaction rate theory, are practically identical for the two isotopic molecules, so that $\kappa_1 = \kappa_2$ and $\delta_1 = \delta_2$. For calculation, all the fundamental vibrational frequencies of the isotopic reactant and activated complex molecules, the ω_i's, would have to be known.

Bigeleisen's equation separates isotope effect into two factors: (1) a "reduced-mass effect" which expresses the effect of mass on the frequency of rupturing or forming the critical bonds in the activated complexes, and (2) a "zero-point energy effect" which expresses the effect of mass change on the equilibrium between the reactant molecules and the activated complexes.

Usually the lighter isotopic molecule will have the greater reaction rate constant. This is because the reduced mass effect factor $(m_2^*/m_1^*)^{\frac{1}{2}}$ is greater than unity (if the subscript 1 refers to the lighter molecule) and because, especially in bond cleavage, the reacting molecules are generally more "tightly bound" than the activated complex molecules, which results in

$$\sum_i^{3N-6} G(u_i)\Delta u_i \text{ being greater than } \sum_i^{3N'-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}.$$

The condition for the heavier molecule to have the greater reaction rate constant, i.e. for a "reverse" isotope effect to occur, according to the Bigeleisen equation, is:

$$\sum^{3N'-6} G_i(u_i^{\ddagger})\Delta u_i^{\ddagger} > \sum^{3N-6} G(u_i)\Delta u_i + \tfrac{1}{2}\ln(m_2^*/m_1^*).$$

The "reverse" C^{14} isotope effect observed in the condensation of *o*-benzoylbenzoic acid appears explicable in terms of the Bigeleisen theoretical treatment on the basis of the reaction mechanism proposed by Newman, if bond formation, equation [3], is the rate controlling step. The two isotopic reactant carbonium ions, species *C*, must be compared with the two corresponding isotopic activated

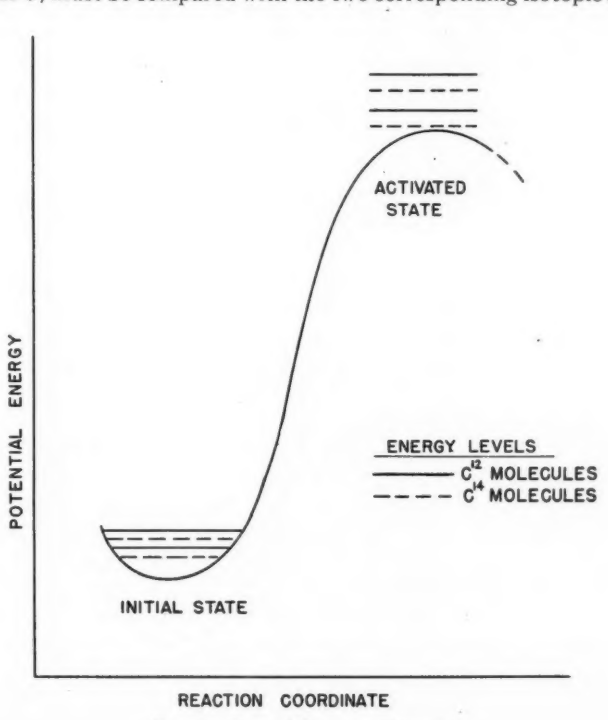


FIG. 2. Potential energy diagram.

complex molecules. Owing to the partial formation of a carbon–carbon bond, an activated complex molecule is then more "tightly bound" than a corresponding reactant molecule. Certain internal rotational degrees of freedom present in the reactant molecule go over into bending vibrational modes in the activated state. The $G(u^{\ddagger})\,\Delta u^{\ddagger}$ terms for these modes can be expected to be larger than the corresponding terms for the reactant molecule. It may be expected therefore that $\sum_i^{3N^1-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}$ will be greater than $\sum_i^{3N-6} G(u_i)\Delta u_i$ for this reaction.

The situation may perhaps be more easily understood in terms of a potential energy curve, Fig. 2. In the initial state, the energy levels of the two isotopic molecules are different, with the levels for the heavier molecule lying below those for the lighter molecules. The same situation holds in the activated state, but because the molecule is now more tightly bound as a result of incipient carbon–carbon bond formation, the energy levels in the activated state are more widely separated than in the initial state.[4] The energy requirement to attain the activated state is therefore greater for the lighter molecules than for the heavier molecules, even though the lighter molecules have the higher energy content in the initial state. The net result is that the concentration of activated complex molecules, relative to reactant molecules, is greater for the heavier isotopic species than for the lighter isotopic species, and the heavier species reacts more rapidly than the lighter species on this account.

The magnitude of the experimental value for the isotope effect, as expressed by the ratio $k(14)/k(12)$, is somewhat surprising, however, for two reasons. Firstly, one might have expected that the "reduced-mass effect" factor, which is a measure of the relative rates of passage of activated complexes over the energy barrier, would counteract the "zero-point energy effect" factor to a large extent. Secondly, it is almost certain that the ratio $K(14)/K(12)$ is less than unity, perhaps having a value as low as 0.95. (This follows from the same argument already given above to hypothesize a higher relative concentration of activated complex molecules for the heavier isotopic molecules than for the lighter isotopic molecules.)

The significant fact is that a value even larger than the experimentally determined 1.07 is indicated for $k^1(14)/k^1(12)$, the reaction rate constant ratio for the unidirectional bond-formation process in this reaction.

One additional point may be worth noting. As previously stated, in the development of the expression for the ratio of reaction rate constants for isotopic molecules, it has been assumed that the transmission coefficients are identical. Calculations (1) using simple hypothetical molecules have shown, however, that transmission coefficients for isotopic molecules can differ appreciably. The possibility that some of the isotope effect observed in this condensation reaction is due to differences in transmission coefficients cannot be ignored even though calculations for this example are completely impractical.

[4]*It might be noted that the departure of the hydrogen atom from a reacting molecule contributes almost exactly the same energy changes to both isotopic molecular species since the hydrogen is attached at an unlabeled position.*

The only logical conclusion which can be drawn from the reverse isotope effect observed, as far as reaction mechanism is concerned, is that bond formation is the rate controlling step in the condensation of *o*-benzoylbenzoic acid to anthraquinone. The mechanism proposed by Newman is thus supported. The measurements are of interest also because only one other "reverse" isotope effect has been reported[5] for C^{14} (12).

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[5]*A "reverse" C^{14} isotope effect reported by Daniels and Myerson (7) was later reported as "normal" (13). The authors understand that reverse isotope effects in a Schmidt reaction and in a pinacol rearrangement were reported by Roe and co-workers at the 124th Meeting of the American Chemical Society in Chicago, September, 1953.*

AN EXAMINATION OF MAYER'S THEORY OF IONIC SOLUTIONS

THE CALCULATION OF THE RELATIVE APPARENT MOLAL HEAT CONTENT AND APPARENT MOLAL VOLUME OF SODIUM CHLORIDE IN AQUEOUS SOLUTIONS AT 25°C.[1]

By G. C. Benson

ABSTRACT

Mayer's theory gives a good representation of the apparent molal volume ϕ_V of sodium chloride in aqueous solution at 25°C. up to a concentration 0.4 molar. Representation of the relative apparent molal heat content ϕ_L is also satisfactory but over a smaller range of concentration. The shape of the ϕ_L curve is strongly influenced by the temperature dependence of the distance of closest approach of oppositely charged ions in the solution. Methods of evaluating this term are considered. The utility of Mayer's theory for the extrapolation of experimental data to infinite dilution is illustrated in the case of ϕ_V and of intermediate heats of dilution.

I. INTRODUCTION

A theory of ionic solutions based on a virial expansion of the osmotic pressure of a solution has been published recently by Mayer (10). The statistical development is similar to that used in treating imperfect gases. A model of hard spherical ions with coulombic interactions in a dielectric continuum is assumed. According to Mayer, the resulting expression for the concentration dependence of the logarithm of the activity coefficient retains terms correct up to and including $c^{3/2}$. Scatchard (16) has discussed the theory in some detail and compared it with the Debye-Hückel theory and its various extensions.

Formulae for the thermodynamic properties of a solution in terms of the Mayer theory have been derived by Poirier (13). In a second paper, Poirier (14) has tabulated the functions necessary for numerical evaluation of these formulae and has applied them to the calculation of the stoichiometric mean ionic molar activity coefficients of several different valence type electrolytes in aqueous solution at 25°C. For sodium chloride, agreement between theory and experiment is good up to about 0.4 molar, where the deviation amounts to 1.5%. The representation for higher valence electrolytes in dilute solution is also quite reasonable, but the discrepancy between theory and experiment becomes noticeable at lower concentrations with increasing complexity of the valence type.

The success of the Mayer theory, as indicated by Poirier's calculations, is sufficient to justify its further examination. In particular, since all the numerical computations have been restricted to activity coefficients at 25°C., an investigation of other thermodynamic properties should be of interest. In this paper, the relative apparent molal heat content ϕ_L and the apparent molal volume ϕ_V of sodium chloride in water at 25°C. are calculated from Mayer's theory. Comparison of the results with experimental data provides a check,

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for a 1–1 electrolyte, on the temperature and pressure dependence predicted by the theory.

The notation and values of the numerical constants employed by Poirier in his two papers (13, 14) have been adopted in the present work and are summarized for convenient reference in the next section. The calculation of ϕ_L is described in Section III and that of ϕ_V in Section IV. This is followed by a discussion of the results in Section V.

II. SUMMARY OF NOTATION AND FORMULAE

In this paper, the set of "natural" variables used to described the thermodynamic state of a two-component system are the temperature, T, external pressure, P, moles of solvent, n_1', and moles of solute, n_2'.[2] Parenthesis with a natural variable written as subscript indicates differentiation of the enclosed quantity with respect to that variable, keeping the other members of the natural set constant.

Mayer's theory leads to the following expressions[3]:

$$[1] \qquad \phi_L = \phi_{H_2} - \phi_{H_2}^\circ = \tau_1 + (\ln a)_T \tau_2,$$

$$[2] \qquad \phi_V = \bar{V}_2^\circ + \omega_1 + (\ln a)_P \omega_2$$

for the relative apparent molal heat content and the apparent molal volume of the solute in an ionic solution at temperature T, pressure P, and concentration c moles per liter.

In equation [1] ϕ_{H_2} and $\phi_{H_2}^\circ$ are the apparent molal heat contents of the solute in the solution at concentration c and at infinite dilution respectively. The quantities τ_1, τ_2, ω_1, and ω_2 are defined by

$$[3] \quad \tau_1 = \nu RT^2 \Big\{ [(\tfrac{1}{3})\alpha_1 + (\ln K)_T + T^{-1}] \ln f'_D - [(\ln K)_T + T^{-1}] \frac{A}{2n_2} \sum_{\mu \geq 0} \frac{(-)^\mu n_\mu^2}{A^\mu} [\mu b_\mu(\varphi) + (\mu - 2) g_\mu(\varphi)] - \alpha_1 \frac{A}{2n_2} \sum_{\mu \geq 0} \frac{(-)^\mu n_\mu^2}{A^\mu} [b_\mu(\varphi) - g_\mu(\varphi)] \Big\},$$

$$[4] \quad \tau_2 = \nu RT^2 \frac{A}{2n_2} \sum_{\mu \geq 0} \frac{(-)^\mu n_\mu^2}{A^\mu} [(3 - \mu) b_\mu(\varphi) - (1 + \mu) g_\mu(\varphi)],$$

$$[5] \quad \omega_1 = \nu RT \Big\{ [(\tfrac{1}{3})\beta_1 - (\ln K)_P] \ln f'_D + \frac{(\ln K)_P A}{2n_2} \sum_{\mu \geq 0} \frac{(-)^\mu n_\mu^2}{A^\mu} [\mu b_\mu(\varphi) + (\mu - 2) g_\mu(\varphi)] - \frac{\beta_1 A}{2n_2} \sum_{\mu \geq 0} \frac{(-)^\mu n_\mu^2}{A^\mu} [b_\mu(\varphi) - g_\mu(\varphi)] \Big\},$$

[2] *Poirier (13, 14) denotes moles of solvent and solute by n_1 and n_2 respectively. A dash has been added to avoid any confusion with the quantities n_μ to be defined later.*

[3] *Equation [2] is a more general form of equation 94 in reference 13 where the $(\ln a)_P$ term has been neglected. Also, an omission appears to have been made in printing equation 94. The first term on the right-hand side should be $[(1/3)\beta_1 - (\ln K)_P] \ln f'_D$ in order that ϕ_V have the Debye-Hückel limiting slope $(2/3)\mathcal{S}_{(V)}$ at high dilutions (see reference 7, pp. 50, 596). This has been confirmed by repeating Poirier's derivation.*

$$[6] \qquad \omega_2 = \nu RT \frac{A}{2n_2} \sum_{\mu>0} \frac{(-)^\mu n_\mu{}^2}{A^\mu} [(\mu - 3)b_\mu(\varphi) + (\mu + 1)g_\mu(\varphi)] = -T^{-1}\tau_2.$$

In equations [1] to [6] the Debye-Hückel limiting expression for the logarithm of the activity coefficient

$$[7] \qquad \ln f'_D = -\frac{n_2 \epsilon^2 \kappa}{2KkT}$$

where

$$[8] \qquad \kappa = \left(\frac{4\pi N_0 \epsilon^2 n_2 \nu c}{1000\, KkT}\right)^{\frac{1}{2}}$$

is used as a convenient parameter. The quantities α_1, β_1, and K are respectively the coefficient of thermal expansion, the coefficient of isothermal compressibility, and the dielectric constant, all for the pure solvent at temperature T and pressure P. $\bar{V}_2{}^\circ$ is the partial molal volume of the solute in an infinitely dilute solution at temperature T and pressure P. The symbols R, k, N_0, and ϵ have their usual meanings (i.e. gas constant per mole, Boltzmann constant, Avogadro's number, and electronic charge, respectively).

A solute molecule dissociates into ν_s ions of type s, each having charge Z_s in protonic units. The total number of ions formed by the dissociation of one molecule is

$$[9] \qquad \nu = \sum_s \nu_s.$$

The quantity n_2 is a special case of the set n_μ defined by

$$[10] \qquad n_\mu = \frac{1}{\nu} \sum_s \nu_s Z_s{}^\mu$$

for all positive integral values of the index μ.

The distance of closest approach of oppositely charged ions in the solution is represented by "a" and is related to the parameters A and φ by the equations

$$[11] \qquad a = \frac{\varphi}{\kappa} = \frac{A\epsilon^2}{KkT}.$$

The functions $b_\mu(\varphi)$, $g_\mu(\varphi)$, and $h_\mu(\varphi)$ are defined by certain definite integrals which have been tabulated (14) numerically at rounded values of φ for μ in the range 0 to 16.

The formula for the logarithm of the stoichiometric mean ionic molar activity coefficient of the solute in the solution at temperature T and pressure P is

$$[12] \qquad \ln f = \ln f' - P_{\text{osm}} [\bar{V}_2{}^\circ / \nu RT + \{\ln f'\}_K (\ln K)_P - \beta_1]$$

where

$$[13] \qquad \ln f' = \ln f'_D - \frac{A}{n_2} \sum_{\mu>0} \frac{(-)^\mu n_\mu{}^2}{A^\mu} b_\mu(\varphi),$$

$$[14] \qquad \{\ln f'\}_K = -(3/2) \ln f'_D + \frac{A}{2n_2} \sum_{\mu>0} \frac{(-)^\mu n_\mu{}^2}{A^\mu} [2\mu b_\mu(\varphi) - g_\mu(\varphi) + h_\mu(\varphi)],$$

and the osmotic pressure is given by

$$[15] \quad P_{osm} = \frac{\nu cRT}{1000}\left\{1 + (\tfrac{1}{3}) \ln f_D' - \frac{A}{2n_2}\sum_{\mu \geq 0} \frac{(-)^{\mu} n_{\mu}^{2}}{A^{\mu}} [b_{\mu}(\varphi) - g_{\mu}(\varphi)]\right\}.$$

The stoichiometric mean ionic molal activity coefficient f_m can be calculated from

$$[16] \quad \ln f_m = \ln f - \ln d_1 - \ln (m/c)$$

where d_1 is the density of the pure solvent and m is the molality corresponding to the molarity c.

The numerical values of the constants taken from Birge (1) and used in the computations of Sections III and IV are

$R = 8.31436 \times 10^{7}$ erg deg.$^{-1}$ mole^{-1} $= 1.98646_{7}$ cal.$_{15}$ deg.$^{-1}$ mole^{-1},
$k = 1.38047_{4} \times 10^{-16}$ erg deg.$^{-1}$,
$N_0 = 6.0228_{3} \times 10^{23}$ mole^{-1},
$\epsilon = 4.8025_{1} \times 10^{-10}$ abs. e.s.u.

The required properties of pure water and of the solute in aqueous sodium chloride solutions are summarized in Table I. For a 1–1 electrolyte n_{μ} is equal to unity for all even values of μ and vanishes for all odd values.

The quantity a which occurs implicitly in the above formulae through A and φ must be treated as a disposable parameter. For sodium chloride in water at 25°C., Poirier (14) used the experimental value of f_m at $m = 0.1$ (given in Table I) in equations [12] to [16] to determine the value of A. The result $A = 0.5464_{1}$ is equivalent to $a = 3.90$ Å. The use of this value in equation [12] gives a reasonable representation of the activity coefficient up to 0.4 molar as mentioned in Section I. Poirier's value for A at 25°C. is adopted in the present calculations.

TABLE I
DATA FOR PURE WATER AND FOR SODIUM CHLORIDE IN AQUEOUS SOLUTIONS

Property	Temperature			Units	Reference
	20°C.	25°C.	30°C.		
Water					
K	80.36_{2}	78.54	76.76_{5}		20
$(\ln K)_T$		$-4.57_{9} \times 10^{-3}$		deg.$^{-1}$	20
$(\ln K)_P$	5.936×10^{-11}	5.854×10^{-11}	5.788×10^{-11}	(dynes/cm.^{2})$^{-1}$	12
β_1	$4.629_{9} \times 10^{-11}$	$4.564_{6} \times 10^{-11}$	$4.514_{3} \times 10^{-11}$	"	4, 12
d_1	0.998234	0.997075	0.995678	gm. ml.$^{-1}$	17
α_1		2.570×10^{-4}		deg.$^{-1}$	17
Aqueous NaCl Solutions					
$\bar{V}_2^{\circ}$	16.20	16.62	16.97	cm.^{3} mole^{-1}	2, 3, 5, 8, 9, 18
$f_m(m = 0.1)$	0.779	0.778	0.777		7, p. 557
$c(m = 0.1)$	0.09964_{0}	0.09951_{7}	0.09938_{4}	mole l.$^{-1}$	7, p. 556

III. THE RELATIVE APPARENT MOLAL HEAT CONTENT OF SODIUM CHLORIDE IN AQUEOUS SOLUTIONS AT 25°C.

The quantities τ_1 and τ_2 in equation [1] can be calculated as functions of the concentration, using the data listed for 25°C. in Table I, along with Poirier's

value of A and tables of the functions $b_\mu(\varphi)$ and $g_\mu(\varphi)$. Complete evaluation of ϕ_L however requires a knowledge of $(\ln a)_T$. A similar term in the Debye-Hückel theory is frequently neglected (6, 12). After a discussion of this quantity, Poirier (13) concludes that there is no reason why $(\ln a)_T$ should be negligibly small, though evaluation of it "is somewhat problematical".

An examination of the results of Harned and Ehlers (6) for aqueous hydrochloric acid solutions indicates that values of $(\ln a)_T$ of the order of 10^{-3} deg.$^{-1}$ are quite possible. The results of assuming $10^4(\ln a)_T = 0, 5, 8, 10, 12, 15,$ and 20 in equation [1] are plotted against $c^{\frac{1}{2}}$ in Fig. 1. For comparison, the Debye-Hückel limiting slope $\frac{2}{3}\mathscr{S}_{(H)}$ (see page 596, reference 7) and the "experimental data"[4] tabulated in reference 7 (see pp. 539–40) are also indicated in this

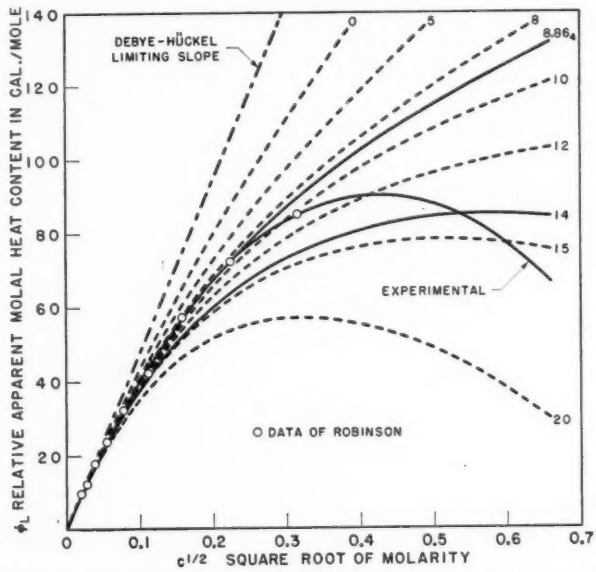

FIG. 1. Relative apparent molal heat content of sodium chloride in aqueous solutions at 25°C. The values of $10^4(\ln a)_T$ are indicated on the calculated curves.

figure. It can be seen that the shape of the ϕ_L curve is quite sensitive to the value of $(\ln a)_T$. Also, it is obviously impossible to reproduce the experimental ϕ_L curve over an extended concentration region such as 0 to 0.4 molar with anything like the success achieved in the case of the activity coefficient. A value of $10^4(\ln a)_T$ in the range 8 to 10 gives a fairly good fit up to 0.1 molar.

After this preliminary examination it is interesting to investigate possible methods of estimating the best value of $(\ln a)_T$ from experimental data. Two distinct ways appear possible. Briefly these are (*a*) through use of experimental data for activity coefficients at other temperatures around 25°C., and

[4]*These data are actually the results of processing experimental heats of dilution in accordance with the Debye-Hückel theory. Later, in Section III of this paper, it is shown that a similar treatment using Mayer's theory leads to essentially the same data.*

(*b*) through the use of experimental heats of dilutions (or equivalent data) at 25°C. These possibilities will be considered in turn.

(*a*) *Determination of* $(\ln a)_T$ *from Activity Coefficient Data at 20° and 30°C.*

At each temperature the value of $\ln f_m$ (for $m = 0.1$) can be calculated using Poirier's tables of $b_\mu(\varphi)$, $g_\mu(\varphi)$, and $h_\mu(\varphi)$ at four round values of φ so chosen that two of the results are greater and two less than the experimental value given in Table I. Lagrangian interpolation at 20°C. leads to $A = 0.5459_3$. A similar calculation at 30°C. gives $A = 0.5469_4$.[5] From these values and $A = 0.5464_1$ at 25°C., $(\ln A)_T$ is found to be 1.8×10^{-4} deg.$^{-1}$ at 25°C. The corresponding value of $(\ln a)_T$ calculated from

[17] $$(\ln a)_T = (\ln A)_T - T^{-1} - (\ln K)_T$$

is

[18] $$(\ln a)_T = [1.8 - 33.5_4 + 45.7_9] \times 10^{-4} = 14.0 \times 10^{-4} \text{ deg.}^{-1}.$$

The plot of ϕ_L against $c^{\frac{1}{2}}$ for $10^4(\ln a)_T = 14$ deg.$^{-1}$ is also shown in Fig. 1. At high dilutions the calculated curve agrees well with the experimental one. Around 0.01 molar the theoretical curve is a few calories per mole lower. This difference increases to 10 cal. mole^{-1} at 0.1 molar and then decreases to zero where the curves cross near 0.3 molar. Above this concentration the theoretical values are higher than the experimental curve. Although $10^4(\ln a)_T = 14$ deg.$^{-1}$ gives a fit to about $\pm 12\%$ up to nearly 0.4 molar, the more empirical calculations outlined at the beginning of this section indicate that a

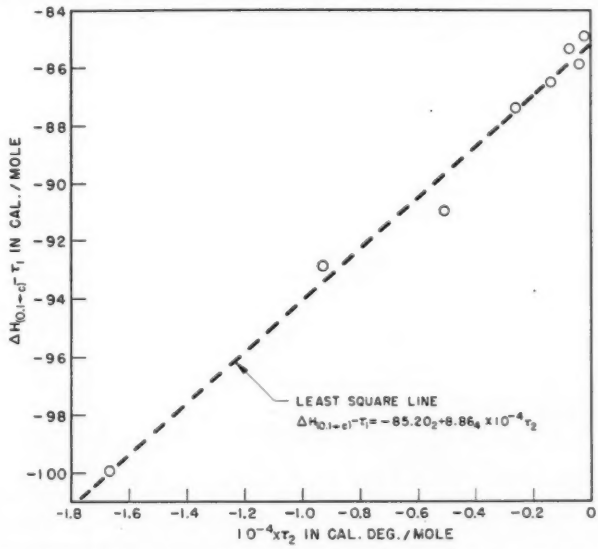

FIG. 2. Extrapolation of intermediate heats of dilution and the determination of $(\ln a)_T$ for aqueous sodium chloride solutions at 25°C.

[5] *Since it is unlikely that a five degree change in temperature will shift the "concentration limit of validity" below 0.1 from the value 0.4 molar established at 25°C. by Poirier, no attempt was made to test the values of A at 20° and 30°C. by comparing calculated and experimental values for the activity coefficient over a range of concentration at each temperature.*

somewhat lower value would give a much better fit over the low concentration range.

(*b*) *Determination of* $(\ln a)_T$ *from Intermediate Heats of Dilution at 25°C.*

The calculation described in part (*a*) does not appear to be a good method of finding the best value of $(\ln a)_T$ since it is subject to large errors resulting from small relative uncertainties in the data employed. Accordingly, it is preferable to evaluate $(\ln a)_T$ more directly from experimental heats of dilution.

From equation [1], $\Delta H_{(0.1\to c)}$ the intermediate heat of dilution from 0.1 molar to concentration c can be written as

[19] $$\Delta H_{(0.1\to c)} - \tau_1 = \phi_{H_2}^{\circ} - \phi_{H_2}(c = 0.1) + (\ln a)_T \tau_2.$$

Employing Robinson's data ((15), see also (7), p. 225) for $\Delta H_{(0.1\to c)}$ at 25°C., the left-hand side of equation [19] is plotted against τ_2 in Fig. 2. The results show a definite linear trend, although some scatter arising from experimental error is apparent. Using the method of least squares the results can be expressed by the linear form

[20] $$\Delta H_{(0.1\to c)} - \tau_1 = -85.20_2 + 8.86_4 \times 10^{-4}\,\tau_2.$$

From the slope and intercept of this line the values

[21] $$10^4(\ln a)_T = 8.86_4 \text{ deg.}^{-1}$$

and

[22] $$\Delta H_{(0.1\to 0)} = -85.20_2 \text{ cal. mole}^{-1}$$

are obtained at 25°C. The relative apparent molal heat content corresponding to $10^4(\ln a)_T$ given by equation [21] has been added to Fig. 1. The resulting curve, as expected, agrees very well with the experimental curve within the experimental error up to about 0.07 molar; beyond this concentration the deviation increases rapidly.

Values of the relative apparent molal heat content determined from Robinson's results extrapolated to zero as just described can be calculated from the equation

[23] $$\phi_L = -\Delta H_{(0.1\to 0)} + \Delta H_{(0.1\to c)} = 85.20_2 + \Delta H_{(0.1\to c)}.$$

These points are also plotted in Fig. 1.

IV. THE APPARENT MOLAL VOLUME OF SODIUM CHLORIDE IN AQUEOUS SOLUTIONS AT 25°C.

In evaluating ϕ_V from equation [2], the quantity $(\ln a)_P$ introduces difficulties similar to those associated with $(\ln a)_T$ in the previous section. Poirier (13) has concluded that $(\ln a)_P$ is quite small and in deriving the formula for ϕ_V assumed that it could be neglected. A similar assumption is usually made in corresponding treatments (11, 12) by the Debye-Hückel theory. However, Wirth and Collier (19) have found that apparent molal volume data for perchloric acid, sodium perchlorate, and hydrochloric acid can be fitted better by using values of $(\ln a)_P = -2.68 \times 10^{-11}$, -0.15×10^{-11}, and -0.7×10^{-11} (dynes/cm.^{2})$^{-1}$, respectively. Accordingly, in the present case $(\ln a)_P$ is retained and the magnitude of it will be chosen to give agreement with experimental results.

Another problem that becomes apparent after a few computations is that the value of $\bar{V}_2^\circ$ at 25°C. used by Poirier (14) and employed so far in these calculations is not consistent with the application of the present theory to available experimental data (9, 18) on the apparent molal volumes of sodium chloride in moderately dilute solutions. The value $\bar{V}_2^\circ = 16.62$ cm.^{3} mole^{-1} has presumably been obtained by extrapolation of a ϕ_V vs. $c^{\frac{1}{2}}$ plot. Owen and Brinkley (12) and Owen (11), investigating the problem from the point of view of the Debye-Hückel theory, concluded that such extrapolations might lead to considerable errors. In the present case the most consistent course is to determine $\bar{V}_2^\circ$ by processing the experimental data in a fashion compatible with Mayer's theory.

In Fig. 3 the difference between the experimental values of ϕ_V and values of ω_1 calculated from equation [5] are plotted against ω_2 calculated from equation

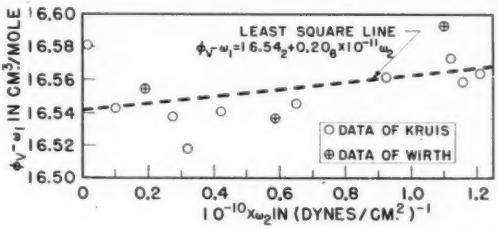

FIG. 3. Extrapolation of the apparent molal volumes of sodium chloride in aqueous solutions at 25°C. to infinite dilution.

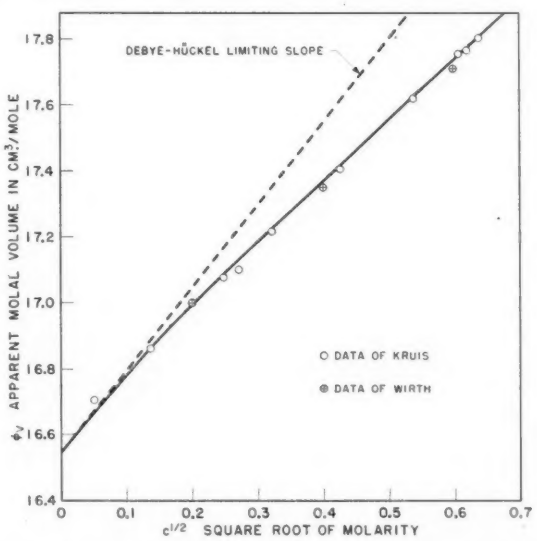

FIG. 4. Apparent molal volume of sodium chloride in aqueous solutions at 25°C. Curve is calculated from Mayer's theory using $\bar{V}_2^\circ = 16.54_2$ cm.^{3} mole^{-1} and $(\ln a)_P = 0.20_8 \times 10^{-11}$ (dynes/cm.^{2})$^{-1}$.

[6]. If the experimental data were perfect and the theory correct, a straight line should result. The equation of the least square line is

$$[24] \qquad \phi_V - \omega_1 = 16.54_2 + 0.20_8 \times 10^{-11}\,\omega_2$$

and from this the values

$$[25] \qquad (\ln a)_P = 0.20_8 \times 10^{-11}\ (\text{dynes/cm.}^2)^{-1},$$

and

$$[26] \qquad \bar{V}_2^\circ = 16.54_2\ \text{cm.}^3\ \text{mole}^{-1}$$

are obtained.[6] The theoretical curve for ϕ_V based on the values given in equations [25] and [26] is plotted against $c^{\frac{1}{2}}$ in Fig. 4. The agreement with experimental data is very good and within experimental error over the whole range up to $c = 0.4$ molar.

V. DISCUSSION

The calculations outlined in the preceding sections indicate that Mayer's theory gives a very satisfactory representation of the apparent molal volume of the solute in aqueous sodium chloride solutions at 25°C. up to the concentration limit of validity (0.4 molar) set by Poirier from a study of activity coefficients. The temperature dependence of the theory is not as good as this, though a good representation of ϕ_L up to about 0.07 molar can be obtained with $10^4(\ln a_T) = 8.86\ \text{deg}^{-1}$.

There is no independent check on the values of $(\ln a)_T$ and $(\ln a)_P$ given in equations [21] and [25]. The maximum of the ϕ_L curve appears to be connected intimately with the term $(\ln a)_T$, though in the present case the theory starts to fail before the maximum is reached. The assumption that $(\ln a)_T = 0$ is quite poor and if heats of dilution or other data are not available to determine $(\ln a)_T$ it would probably be better to assume $(\ln A)_T = 0$ (see equation [18]). The value of $(\ln a)_P$ is small and, though comparable in magnitude, has the opposite sign to values for other electrolytes obtained by Wirth and Collier (19) from an application of the Debye-Hückel theory. The quantity ω_2 is approximately proportional to c and at $c = 0.4$ molar the term $(\ln a)_P\,\omega_2$ makes a contribution of only 0.02_5 cm.^{3} mole^{-1} to ϕ_V.

It appears that Mayer's theory may be of use in extrapolating experimental data to infinite dilution. This has been illustrated for $\Delta H_{(0.1\to c)}$ and for ϕ_V. If only the intercept is required it is sufficient to replace the abscissae in Figs. 2 and 3 by c since τ_2 and ω_2 are approximately proportional to the molarity. The values resulting from these extrapolations are in good agreement with the most recent extrapolations based on the Debye-Hückel theory by Owen and

[6] *It does not seem possible to reconcile the previous value $\bar{V}_2^\circ = 16.62$ with the data treated in this way. If, instead of determining the least square line, an arithmetic mean is taken of $\phi_V - \omega_1$ the value of $\bar{V}_2^\circ$ is 16.55_2 cm.^{3} mole^{-1}.*

The osmotic correction term in equation [12] is strongly dependent on $\bar{V}_2^\circ$; however the whole contribution of this term to $\ln f$ at 0.1 molar is only about $\frac{1}{2}\%$ and variations due to a decrease of $\frac{1}{2}\%$ in $\bar{V}_2^\circ$ will have a negligible effect on the previous calculations and in particular on the value used for A.

Brinkley (12)—(see also reference 7, pp. 595–9). These authors obtained the values $\bar{V}_2^\circ = 16.538$ cm.^{3} mole^{-1} and $\Delta H_{(0.1\to 0)} = -85.0_1$ cal. mole^{-1}.[7]

Evidently ϕ_{H_s} and ϕ_V for sodium chloride solutions at 25°C. can be represented by either Mayer's theory or the Debye-Hückel theory with very nearly equal success; however, the following difference should be noted. In the present work based on Mayer's theory the terms $(\ln a)_T$ and $(\ln a)_P$ are retained and must be treated as adjustable parameters since independent evaluation is not available. In the calculations of Owen and Brinkley (12, see equations 32 and 31) both $(\ln a)_T\,\theta c$ and $(\ln a)_P\,\theta c$ are put equal to zero but terms $\frac{1}{2}K_H c$ and $\frac{1}{2}K_V c$ are retained. K_H and K_V can be related to the B-coefficient (and its temperature and pressure derivatives) of the empirical linear term in the Debye-Hückel expression for the activity coefficient (see equations 3–8–8 and 3–9–5 of reference 7) but must also be treated as adjustable parameters. Since θ can be expressed as a power series in κa with leading term unity (12, see equation 24a), the procedure used by Owen and Brinkley may partially retain the $(\ln a)_T$ and $(\ln a)_P$ terms hidden in the coefficients K_H and K_V. From this point of view, the terms of the representation by Mayer's theory are more closely related to the theoretical model than in the corresponding Debye-Hückel treatment.

Although it is dangerous to generalize on the basis of the single example studied in this paper, the above conclusions are probably applicable to other 1–1 electrolytes and in a more restricted range to higher valence types.

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[7] *Equation 44 of reference 12 appears to contain a misprint which has been copied in equation (B-4-10) of reference 7. The value attributed above to Owen and Brinkley was calculated at $c = 0.1$ from their equation 44 rewritten as*

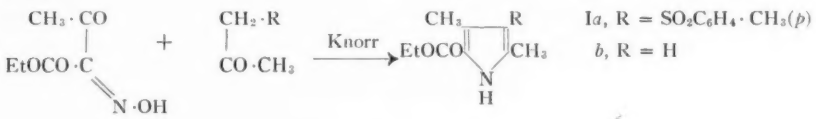
$$\phi_H - \phi_H^\circ = 471.8\,\Omega_H\,c^{\frac{1}{2}} - 217c.$$

A MODIFIED KNORR PYRROLE SYNTHESIS*

By S. F. MacDonald and R. J. Stedman

Intermediates for the synthesis of porphyrins are obtained by combining isonitroso-ketoesters with ethyl, benzyl, or *t*-butyl acetoacetates in the Knorr synthesis, and converting the products into pyrroles with a free β position by partial hydrolysis and pyrolysis (2), catalytic debenzylation and pyrolysis (3), or pyrolysis (5), respectively.

Another modification has been found in which isonitrosoacetoacetic ester and *p*-toluenesulphonylacetone are combined in the Knorr synthesis to give I*a* in 4% yield. Although this was converted into I*b* in 76% yield by Raney nickel desulphurization, the method was not extended beyond this model in view of the low yield in the Knorr synthesis. The method would be useful in cases where the high temperature necessary for decarboxylation was to be avoided.



Ia, R = $SO_2C_6H_4 \cdot CH_3(p)$
b, R = H

EXPERIMENTAL

p-Toluenesulphonylacetone

A 54% yield of recrystallized product m.p. 51–52° was obtained according to Otto and Otto (4).

2,4-Dimethyl-3-p-toluenesulphonyl-5-carbethoxypyrrole (*Ia*)

Sodium nitrite (7.5 gm.) in a little water was added to ethyl acetoacetate (13 gm.) in acetic acid (30 cc.) at 4–8° and the excess nitrite destroyed with ammonium sulphamate. After the addition of acetic acid (70 cc.), ammonium acetate (15 gm.), and *p*-toluenesulphonylacetone (21.2 gm.), the mixture was warmed to 60° and held at that temperature by cooling and stirring while zinc dust (30 gm.) was added in portions. After a further 15 min. the solution was decanted into ice water (2 liters) and the zinc washed with acetic acid (50%, then glacial). After four hours at 0°, the precipitate was collected, washed with *N* sodium hydroxide to remove unchanged sulphone and zinc salts, dried, and extracted with petrol ether (b.p. 60–75°) (thimble) to remove 2,4-dimethyl-3,5-dicarbethoxypyrrole. When the residue was extracted with ethanol (thimble), the extract concentrated to 20 cc. and kept at 0°, the pyrrole (1.2 gm., 4%) separated as small colorless plates, m.p. 185–186°, unchanged by recrystallization. Ehrlich's reaction was positive hot. Calc. for $C_{16}H_{19}O_4NS$:

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C, 59.79; H, 5.96; N, 4.36; S, 9.98%. Found in material dried at 100° *in vacuo*: C, 59.87; H, 6.15; N, 4.38; S, 9.94%.

2,4-Dimethyl-5-carbethoxypyrrole (*Ib*)

The pyrrole sulphone (1.22 gm.) was refluxed for four hours with freshly prepared W-6 catalyst (1) (20 cc.) in absolute ethanol (60 cc.). The catalyst was separated and washed by centrifuging, and the ethanol evaporated. The residue was extracted with petrol ether (b.p. 60–75°, 50 cc.) (thimble), giving the pyrrole as colorless prisms (0.342 gm.) m.p. 123–124° on cooling of the extract; concentration gave a second crop (0.143 gm.; total 76%) m.p. 122.5–123.5°. Both crops gave a positive Ehrlich's reaction cold, and did not depress the melting point of authentic material of m.p. 123–124°. Calc. for $C_9H_{13}O_2N$: C, 64.65; H, 7.83; N, 8.38%. Found in material recrystallized from hexane and dried *in vacuo*: C, 64.44; H, 7.54; N, 8.37%; Lassaigne test for sulphur, negative.

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ORGANIC DEUTERIUM COMPOUNDS
XII. BENZENE-d_6*

BY L. C. LEITCH

Several methods of preparing benzene-d_6 were reviewed and evaluated by Ingold and Wilson (3). These authors reported that the exchange reaction between benzene and 50 mole % deuterium sulphate – deuterium oxide solution gave benzene-d_6 of higher deuterium content than any other method. They pointed out that the nickel catalyzed vapor phase exchange between benzene and deuterium oxide discovered by Horiuti and Polanyi (2) and developed by Bowman, Benedict, and Taylor (1) gave benzene-d_6 which contained 14 mole % C_6D_5H.† Notwithstanding this criticism by Ingold and Wilson, it seemed desirable to reinvestigate the heterogeneous exchange reaction between benzene and deuterium oxide on account of its simplicity. After exchanging benzene four times with deuterium oxide at 110°C. in the presence of platinum black, a product was obtained which contained less than 4 mole % C_6D_5H and was 99.2% deuterated. Such material is satisfactory for most purposes. The advantages of the present method are that the reaction

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†*Shortly after this paper had been submitted for publication Dixon and Schiessler (J. Am. Chem. Soc. 76: 2197. 1954) reported the method of preparation of benzene-d_6 of Ingold and Wilson (3) to be superior to that of Bowman, Benedict, and Taylor (1).*

time is shortened and the rather tedious preparation of deuterium sulphate is avoided.

EXPERIMENTAL

Benzene-d_6

A mixture of benzene (5.0 ml., previously dried and distilled over sodium), deuterium oxide (10.0 ml., 99.5%), and platinum black (0.3 gm., prepared by reducing Adams' catalyst with deuterium) was heated in a sealed tube with a re-entrant joint in a rocking furnace for 12 hr. at 110°C. After the tube had been opened with a magnetic hammer while attached to a vacuum line the deuterated benzene was fractioned and then distilled through a U-tube containing Drierite into a trap. The benzene was recovered nearly quantitatively. A small sample was removed for mass spectrometric analysis and the balance was distilled into another reaction tube containing platinum black and fresh deuterium oxide. This operation was repeated twice more. The deuterium content after each exchange is shown in Table I.

TABLE I
DEUTERIUM CONTENT IN MOLE PER CENT AFTER EACH EXCHANGE

	1st	2nd	3rd	4th
C_6D_6	19.8	65.6	86.7	95.24
C_6D_5H	42.7	31.8	12.0	3.96
$C_6D_4H_2$	37.6	3.18	2.4	—

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